PB86-120326

Evaluation of Sampling and Analytical Methodology for Polynuclear Aromatic Compounds in Indoor Air

Battelle Columbus Labs., OH

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Oct 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-120326

EPA/600/4-85/065
October 1985

EVALUATION OF SAMPLING AND ANALYTICAL METHODOLOGY FOR POLYNUCLEAR AROMATIC COMPOUNDS IN INDOOR AIR

by

C. C. Chuang, G. A. Mack, P. J. Mondron,
and B. A. Petersen
Battelle Columbus Division
Columbus, Ohio 43201

Contract Number 68-02-3437

Project Officer

Nancy K. Wilson
Methods Development and Analysis Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/4-85/065		

4. TITLE AND SUBTITLE
Evaluation of Sampling and Analytical Methodology for Polynuclear Aromatic Compounds in Indoor Air

5. REPORT DATE
October 1985

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
C. C. Chuang, G. A. Mack, P. J. Mondron and B. A. Petersen

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Battelle Columbus Division
505 King Avenue
Columbus, Ohio 43201

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-3487, Task 26

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final 3/1/83 to 9/30/83

14. SPONSORING AGENCY CODE
EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The objective of this project was to develop a generic sampling and analytical methodology to characterize the polynuclear aromatic hydrocarbon (PAH) concentrations in air within various microenvironments. The following three studies were performed: evaluation of analytical methods, design of a sampling method, and design of a pilot study. Two analytical methods, high performance liquid chromatography with ultraviolet adsorption and fluorescence detection and gas chromatography/mass spectrometry, were evaluated for the determination of PAHs and their derivatives in air within microenvironments. The results showed that gas chromatography/positive chemical ionization mass spectrometry with data acquisition in the selected ion monitoring mode is the preferred analytical approach. A modified EPA high volume sampler, consisting of a quartz fiber filter and a polyurethane foam cartridge, is proposed for use in a future experimental study. A literature review was conducted to determine what is known about the contribution of cigarette smoke to the levels of PAHs in air within microenvironments and to evaluate the use of quinoline and isoquinoline as possible marker compounds for the levels of cigarette smoke. A pilot study was designed to assess PAH levels in air found in residences. A study using this design will be conducted in Columbus, Ohio, during the winter of 1983/84. These results can then be applied to a future large-scale study involving the measurement of human exposure to PAH in air.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	93
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-02-3487 to Battelle. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for assessment of environmental monitoring technology and systems, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of human exposure to toxic organic compounds is an area of increasing significance to EPA. The sampling and analytical methodology described in this report provides an important step toward measurement of, and understanding the extent of human exposure to, an important class of chemicals--the polynuclear aromatic compounds--in air.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ABSTRACT

The objective of this project was to develop a generic sampling and analytical methodology to characterize the polynuclear aromatic hydrocarbon (PAH) concentrations in air within various microenvironments. The following three studies were performed: evaluation of analytical methods, design of a sampling method, and design of a pilot study.

Two analytical methods, high performance liquid chromatography with ultraviolet absorption and fluorescence detection and gas chromatography/mass spectrometry, were evaluated for the determination of PAHs and their derivatives in air within microenvironments. This evaluation compared the sensitivity, selectivity, specificity, and speed of response of these two analytical methods. The results showed that gas chromatography/positive chemical ionization mass spectrometry with data acquisition in the selected ion monitoring mode is the preferred analytical approach.

A modified EPA high volume sampler, consisting of a quartz fiber filter and a polyurethane foam (PUF) cartridge, is proposed for use in a future experimental study. A generic sampling procedure was developed that can be used to collect PAHs at various sampling sites. The ranges for the following sampling parameters were established in this project: sampling volume, 100 m^3; sampling time, 8 hr; sampling temperature, $\leq 20^{o}C$; sampling flow rate, 15-20 m^3/hr; filter face velocity, 30-40 m/min; filter capacity for particles, very high, (typically ≤ 1 g for 4 in. diameter filter).

A literature review was conducted to determine what is known about the contribution of cigarette smoke to the levels of PAHs in air within microenvironments and to evaluate the use of quinoline and isoquinoline as possible marker compounds for the levels of cigarette smoke. This review found considerable information on the levels of PAHs in cigarette smoke condensate, but only a few studies of the PAH concentrations in air within microenvironments that are occupied by smokers. Quinoline and isoquinoline are the most abundant aza-arene compounds in cigarette smoke condensate, but these compounds are also found in coal combustion emissions, air particulate matter, and automobile exhaust. This finding suggests that quinoline and isoquinoline may not be appropriate marker compounds for cigarette smoke.

Based on the evaluation of analytical and sampling methodology, a pilot study was designed to assess PAH levels in air in residences. A study using this design will be conducted in Columbus, Ohio, during the winter of 1983/84. Background information for the determination of the PAH concentration in air within residences can be established from this study. This information can then be applied to a future large-scale study involving the measurement of human exposure to PAH in air.

This report was submitted in fulfillment of Contract No. 68-02-3487 by Battelle under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from March 1, 1983, to September 30, 1983, and work was completed as of January 31, 1984.

CONTENTS

Foreword iii
Abstract iv
Figures viii
Tables ix
Abbreviations x
Acknowledgment xi

1. Introduction 1
2. Conclusions 3
3. Recommendations 5
4. Evaluation of Analytical Methodology for PAH in Air 6
   - Introduction 6
   - Experimental Procedures 7
   - Analysis of Target Compounds by Gas Chromatography/Mass Spectrometry 10
   - Analysis of Target Compounds by High Performance Liquid Chromatography 15
   - Comparison of Positive Chemical Ionization Gas Chromatography/Mass Spectrometry and High Performance Liquid Chromatography Methods for Analysis of Target Compounds 17
5. Development of Sampling Methodology 20
   - Introduction 20
   - Sampling Methodology 20
6. The Influence of Cigarette Smoke on the Polynuclear Aromatic Compound Concentration in Air in Microenvironments 24
   - Introduction 24
   - PAH Profiles in Cigarette Smoke 24
   - Quinoline and Isoquinoline Concentrations in Cigarette Smoke Condensate 26
7. Design of a Pilot Study 27
   - Introduction 27
   - Selection of Sample Residences 27
   - Sampling Periods and Locations 29
   - Data to be Collected 30

References 33

Appendices

A. Total Ion Current Chromatograms from NCI, PCI, and EI GC/MS Analysis of the Air Particulate Extract Samples 36
B. Chromatograms from HPLC Analysis of the Air Particulate Extract Samples 74

FIGURES

Number		Page
1	Diagram of the procedure for the fractionation and analysis of target compounds in the air particulate extract	9
2	Design for selection of the experimental homes	29
3	Overview of the experimental design for the range-finding study. . .	32

TABLES

Number		Page
1	Concentrations of Target Compounds in the High and Low Level Standard Solutions	8
2	GC/MS Operating Conditions	12
3	The Estimated Detection Limits for the Target Compounds Using GC/MS Methods	13
4	Recovery of Target Compounds in the CH_2Cl_2 Fraction Through the Silica Gel Clean-Up Procedure	15
5	HPLC Operating Conditions	16
6	Comparison of Analytical Methods	18
7	Parameters for a Generic Sampling Procedure for Air in Microenvironments	22

LIST OF ABBREVIATIONS

CSC	Cigarette smoke condensate
EI	Electron impact
GC/MS	Gas chromatography/mass spectrometry
HPLC	High performance liquid chromatography
MID	Multiple ion detection
NCI	Negative chemical ionization
PAH	Polynuclear aromatic hydrocarbon
PCI	Positive chemical ionization
PUF	Polyurethane foam
RIC	Reconstructed ion chromatogram
SIM	Selected ion monitoring
UV	Ultraviolet

ACKNOWLEDGMENT

The financial support, and the encouragement and direction of Dr. Nancy K. Wilson of the U.S. Environmental Protection Agency, are gratefully acknowledged.

SECTION 1

INTRODUCTION

The overall objective of this project was to develop sampling and analytical methodology that can be used to study human exposure to polynuclear aromatic compounds and their derivatives in air in microenvironments. The microenvironments of greatest importance are those where people spend most of their time. They include residences, work places, and commuting routes. Therefore, in this work, generic sampling and analytical methodology was designed to characterize the polynuclear aromatic compound (PAH) concentrations in air within a wide variety of microenvironments.

In the course of development of such generic methodology, four aspects had to be addressed: evaluation of the analytical methodology for measurement of PAH in air, development of sampling methodology, characterization of the influence of cigarette smoke on the PAH concentration in microenvironments, and design of a pilot study.

In the first three parts of this project, investigations were conducted to select analytical and sampling methods for an experimental study. In the fourth part a preliminary study was designed, the results of which can be used to test the generic monitoring procedure prior to conducting a larger experimental study.

In the recently completed literature review of sampling and analytical methodology for PAH in air (1), a series of polynuclear aromatic hydrocarbons was recommended for measurement to characterize PAH in ambient air. Nitropyrene was also selected for study because it is extremely mutagenic and has been identified in extracts of urban air particle samples. To assess the contributions of PAH from tobacco smoke to the total PAH levels, particularly within residences, quinoline and isoquinoline were selected as possible markers. The target compounds for this study are presented in the following list.

Species	Class
Phenanthrene	PAH
Fluoranthene	PAH
Pyrene	PAH
Cyclopenta(c,d)pyrene	PAH
Benz(a)anthracene	PAH
Benzo(e)pyrene	PAH
Benzo(a)pyrene	PAH
Benzo(g,h,i)perylene	PAH
Coronene	PAH
1-Nitropyrene	Nitro-PAH
Quinoline	Nitrogen heterocycle
Isoquinoline	Nitrogen heterocycle

In the first part of this work, high performance liquid chromatography with ultraviolet absorption and fluorescence detection (HPLC) and gas chromatography/mass spectrometry (GC/MS) were evaluated for the determination of the target compounds in the three compound classes given above. In the second part, generic sampling methodology for various types of microenvironments was developed. Based on the results from the analytical methodology evaluation, the quantity of analyte necessary for an accurate measurement was estimated. Sampling parameters to collect the necessary quantity of material for analysis were then established. In the third part, a literature survey was made to determine what was known about the influence of cigarette smoke on the PAH concentration in microenvironments, and about the use of quinoline and isoquinoline as evidence of the level of PAH from cigarette smoke. Only a few studies in the literature involved the determination of PAH concentrations in air in residences. The work performed in the fourth part of this study was the design of a study to determine the range of PAH contamination in residential air.

SECTION 2

CONCLUSIONS

The results of the evaluation of analytical methodology showed that the high performance liquid chromatography with ultraviolet absorption and fluorescence detection (HPLC) did not detect all the target compounds under one analytical condition. At least two analyses, one analysis for nitrogen heterocyclic compounds and one analysis for nitropyrene and PAHs, are required for the determination of all the target compounds by the HPLC method. In addition, further sample clean-up is necessary to perform quantitative analysis using this method on air particulate extracts. Although negative chemical ionization gas chromatography/mass spectrometry (NCI GC/MS) has been demonstrated to be the most sensitive technique for the determination of nitropyrene, this method does not provide adequate sensitivity and selectivity for all the target compounds. A clean-up procedure is required for analyzing all the target compounds in an air particulate extract using NCI GC/MS. Both the positive chemical ionization (PCI) and electron impact (EI) GC/MS methods are adequate for determination of all the target compounds. The difference between the EI and the PCI method is that the PCI method is at least 10 times more sensitive for nitrogen heterocyclic compounds. Therefore, if the nitrogen heterocyclic compounds are to be measured, the HPLC, NCI GC/MS, and EI GC/MS methods are not appropriate to use for the determination of the target compounds, and the PCI GC/MS method is the recommended analytical methodology for the future experimental study.

Several important sampling parameters were established in this study and are summarized as follows:

Parameter	Conditions
Sampler configuration	A modified high volume sampler consisting of a filter and a PUF backup trap
Sampling volume	100 m^3
Sampling time	8 hr
Sampling temperature	$\leq 20^oC$
Sampling flow rate	15-20 m^3/hr
Filter face velocity	30-40 m/min
Filter capacity for particles	Very high
Frequency of sampling	Depends on the study design
Number of sampling events per site	Depends on the study design

Based on these sampling parameters, a generic sampling methodology has been developed and can be used to collect PAH compounds in various micro-environments.

The results of the literature survey showed that all the target compounds except nitropyrene have been detected in cigarette smoke condensate. The concentrations of PAHs in air within a microenvironment in which cigarettes are being smoked are higher than levels of PAHs typically found in ambient air. It is concluded that cigarette smoking may be a significant contributor to PAHs found in air within microenvironments. The survey also indicated that quinoline and isoquinoline are the most abundant aza-arene compounds found in cigarette smoke condensate, but that these compounds also have been detected in coal combustion emission, ambient air particulate matter, and automobile exhaust emission. Therefore, quinoline and isoquinoline may not be appropriate marker compounds for cigarette smoking.

SECTION 3

RECOMMENDATIONS

Based on the results of this study, the following three recommendations can be made.

The on-column injection, positive chemical ionization, gas chromatography/mass spectrometry (PCI GC/MS) technique with data acquisition in the selected ion monitoring mode has been demonstrated to provide adequate sensitivity, selectivity, specificity, and speed of response for the determination of all the target compounds. Therefore, use of the PCI GC/MS method is strongly recommended for analysis of the target compounds in the future pilot study.

A modified high volume sampler, consisting of a quartz fiber filter to collect particulate matter and a polyurethane foam cartridge to collect vapor is recommended for evaluation and development for use in the future study. Studies are recommended to determine the retention characteristics of PUF cartridges for PAHs and to develop the analytical method to remove PAHs from the PUF cartridges.

The results of the literature survey showed that cigarette smoking may contribute significantly to the levels of PAHs in air within micro-environments. Therefore, cigarette smoking is recommended for consideration as an experimental factor in the pilot study. The survey also indicated that quinoline and isoquinoline may not be appropriate marker compounds for cigarette smoking. However, these compounds should still be included in the pilot study to determine whether these two compounds can be used as tracers for cigarette smoking.

SECTION 4

EVALUATION OF ANALYTICAL METHODOLOGY FOR PAH IN AIR

INTRODUCTION

The objective of this study was to evaluate existing analytical methods for the measurement of the 12 target compounds within 3 compound classes listed in Section 1 of this report. The criteria selected for evaluation are:

Detection limit -- Determination of the lowest quantity necessary for measurement. Also referred to as sensitivity in this report.

Selectivity -- Determination of the ability of the technique to distinguish species within a compound class and species in different compound classes.

Specificity -- Determination of the ability of the procedure to identify and quantify specific compounds in complex mixtures.

Speed of response -- Determination of the total analysis time.

Based on the results and recommendations of a state-of-the-art review (1), high performance liquid chromatography with ultraviolet absorbance and fluorescence detectors (HPLC) and gas chromatography/mass spectrometry (GC/MS) have the ability to determine PAHs qualitatively and quantitatively in complex matrices. These two techniques potentially satisfied requirements for the criteria listed above and were chosen for evaluation.

Analyses of standards containing all the target compounds using both techniques (HPLC and GC/MS) were performed to assess the sensitivity and selectivity of each technique. To evaluate the specificity of each technique, nonfractionated and fractionated air particulate extracts were also analyzed by both analytical methods. The purpose of these analyses was to examine the influence of other classes of compounds present in air particulate extracts on the detection of the target compounds. To determine any improvement in specificity due to compound class isolation, the air

particulate extract was fractionated into nonpolar, moderately polar, and highly polar fractions before analysis. The target compounds were expected to be in the moderately polar fraction. By removal of the nonpolar (aliphatic) and highly polar (oxygenated) organic compounds, the sensitivity and selectivity of the techniques evaluated could also be significantly improved. Evaluation of the speed of response for the analysis requires consideration of the sensitivity, the number of analyses that are required to determine the target compounds, and the total sample preparation time. Based on the information obtained in the above analyses of standards and air particle extracts, an estimate of the speed of response for each procedure can be established. Experimental procedures and discussions of the analysis of target compounds by both techniques are detailed in the following section.

EXPERIMENTAL PROCEDURES

Preparation of Standard Solutions

About 1 mg of each target compound was placed on a tared aluminum weighing disk and was weighed on a Mettler ME-30 microbalance. The weighed compound was transferred to a 10 mL volumetric flask and the weighing disk was rinsed with small amounts of methylene chloride to ensure that all the material was transferred into the flask. After all the selected compounds were weighed and transferred, methylene chloride was added to the flask to a total volume of 10 mL. Thus, the concentration of this stock standard solution is ~100 ng/µL for each compound.

A 1 mL aliquot was transferred to another 10 mL volumetric flask and diluted to 10 mL. The diluted solution was designated as high level standard solution, at a concentration level of ~10 ng/µL for each compound. The low level standard solution (~1 ng/µL) was prepared by diluting a 100 µL aliquot of the stock solution to a final volume of 10 mL. The exact concentrations of the high and low level standards are listed in Table 1.

Silica Gel Fractionation Procedure

A fractionation method has been developed by Battelle (2) to separate complex organic extracts of diesel particulate matter and ambient air particulate matter into different compound classes. The open column

TABLE 1. CONCENTRATIONS OF TARGET COMPOUNDS IN THE HIGH AND LOW LEVEL STANDARD SOLUTIONS

Compound	Concentration, ng/μL	
	High Level	Low Level
Phenanthrene	11.9	1.19
Fluoranthene	12.4	1.24
Pyrene	10.6	1.06
Cyclopenta(c,d)pyrene(a)	~3	0.3
Benz(a)anthracene	12.2	1.22
Benzo(e)pyrene	11.3	1.13
Benzo(a)pyrene	10.5	1.05
Benzo(g,h,i)perylene	9.3	0.93
Coronene	10.9	1.09
1-Nitropyrene	10.3	1.03
Quinoline	10.4	1.04
Isoquinoline	10.4	1.04

(a) Only limited amounts of cyclopenta(c,d)pyrene were available.

chromatographic techniques used in this fractionation scheme were not limited by sample size. Larger or smaller quantities of elution solvent were expected to produce the same compound class separation for a large range of sample sizes. This method has previously been applied to extracts containing as little as 1 mg to as much as 1 g of extractable organic material.

A schematic representation of the fractionation procedure used in this program is shown in Figure 1.

An aliquot (13.2 mg) of a stored air particulate extract was removed and diluted with 10 mL methylene chloride and then divided into two equal portions. Portion one was designated as a background sample without spiking any of the target compounds. Portion two was spiked with 100 μL of the high

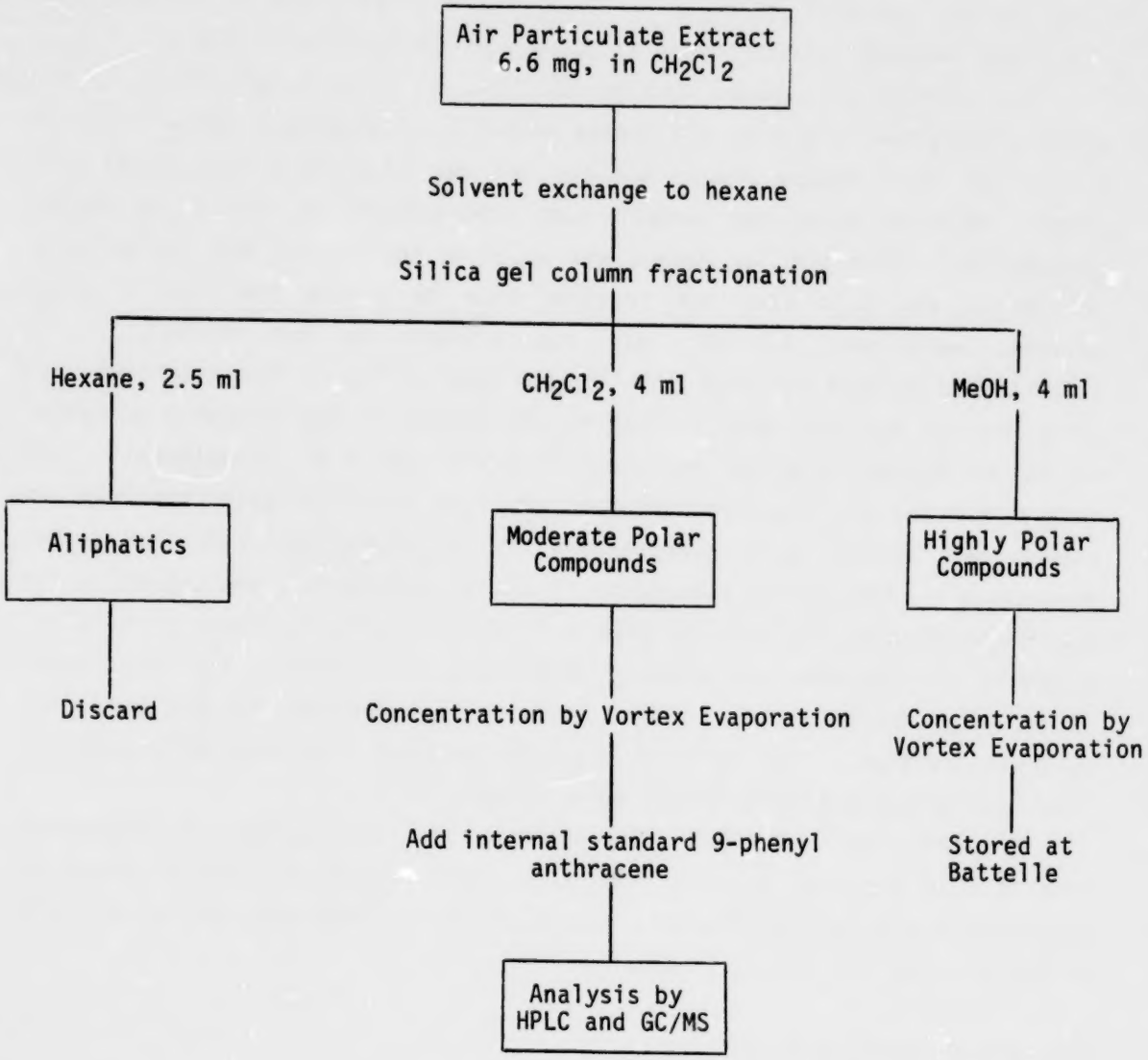

Figure 1. Diagram of the procedure for the fractionation and analysis of target compounds in the air particulate extract

level target compound standards. These two extracts were to be separated into three compound classes using silica gel column chromatography.

The silica gel column (~0.55 cm I.D. x 7 cm length in a 6-inch disposable Pasteur pipette) was packed with 1 g of 5 percent H_2O-deactivated silica gel in a hexane slurry and the gel was retained with a glass wool plug. Each of these two samples was concentrated to 200 µL by Vortex evaporation. Then 1 mL of hexane was added to the extract and concentrated to 200 µL, and this step was repeated once to ensure that the original solvent, methylene chloride, was not present in the extract. The concentrated extract was then added to the head of the silica gel column and three elution solvents were applied to the column in the following sequence: 2.5 mL of hexane, 4 mL of methylene chloride and 4 mL of methanol. The hexane fraction was discarded and the remaining fractions generated from the silica gel column were concentrated to approximately 1 mL by Vortex evaporation. The internal standard, 9-phenyl anthracene, was added to the methylene chloride fraction to give a final concentration level of 5 ng/µL. Aliphatic hydrocarbons are present in the hexane fraction. The PAHs, mono-nitro-PAHs, and moderately polar compounds are present in the methylene chloride fraction. The methanol fraction contains PAHs with more than one functional group and other highly polar compounds.

The methylene chloride fractions from both the spiked and non-spiked samples were analyzed by HPLC with ultraviolet absorption and fluorescence detectors and GC/MS techniques. The methanol fraction were stored at -70°C in the dark for any future chemical analysis.

ANALYSIS OF TARGET COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

The high and low level standard solutions, nonfractionated stored air particulate extract, and methylene chloride fractions (with and without spiking standards) were analyzed by GC/MS with negative chemical ionization (NCI), positive chemical ionization (PCI), and electron impact (EI) conditions. These samples and standards were analyzed in both selected ion monitoring (SIM) and full scan modes.

A standard Finnigan Model 4500 GC/MS with a Carlo Erba on-column injector was used for these analyses. An Ultra No. 2 cross-linked 5 percent phenyl methyl silicone fused silica capillary column was used as both the GC column and the transfer line to link the gas chromatograph and the mass spectrometer. Data collection and processing utilized a Finnigan INCOS 2100 data system. The GC/MS operating conditions are given in Table 2.

Analysis of Target Compounds by Negative Chemical Ionization Gas Chromatography/Mass Spectrometry

The results of the negative chemical ionization (NCI) method showed that this is the most sensitive technique for the determination of nitropyrene, fluoranthene, cyclopenta(c,d)pyrene, benzo(a)pyrene, and benzo(g,h,i)-perylene. However, this method cannot detect certain target compounds such as quinoline, isoquinoline, phenanthrene, pyrene, benz(a)anthracene, benzo(e)pyrene, and coronene in 10-ng quantities on-column in the full scan mode. This may be because the detection capability of the NCI method is highly dependent upon the structure of the individual compound. If a compound is highly electronegative, such as a compound with nitro substitution, it is susceptible to the attachment of a thermal electron from the reagent gas plasma, which lowers the detection limit. The results showed that the silica gel clean-up steps are required for analyzing the target compounds in an air particulate extract by the NCI method. This observation indicated that highly polar compounds present in the air particulate extract may be sensitive to NCI and interfere with the analysis of the target compounds. Due to cost limitations, the actual detection limits of the target compounds were not calculated. Detection limits for the analysis of the target compounds were estimated, based on the results of the low level standard solution analyses, and were established from the following considerations:

- Measure the ratio (Rp) of the signal to the noise level from the low level standard analysis (~1ng on column)
- Set the ratio (Rd) of the signal to the noise level to 3 for the detection limit

TABLE 2. GC/MS OPERATING CONDITIONS

GC Parameters	
Column	Ultra No. 2 fused silica, cross-linked 5% phenyl methylsilicone, 50 m x 0.31 mm I.D., 0.52 μm film (Hewlett-Packard)
Carrier	CH_4, velocity 50 cm/sec at 250°C
Sample Injection	1-2 μL, on-column mode
Program	45°C; 1 min; ballistically to 150°C, 3 min; 150°C to 320°C at 6°C/min; hold for 20 min.
MS Parameters	
Interface	320°C; fused silica column directly introduced into ion source
Mass Scan	45 to 450 amu at 1 sec/scan in EI mode 100 to 450 amu at 1 sec/scan in PCI and NCI modes
Filament Emission Current	0.3 ma
Signal Amplifications	10^{-7} amp/volt with 10^5 electron multiplier gain
EI Conditions	70 eV
PCI Conditions	CH_4 at ~1.0 torr; 150 eV
NCI Conditions	CH_4 at ~1.0 torr; 200 eV
Ionizer Temperature	180°C

- The estimated detected limit (ng on-column) can then be calculated by the ratio of Rd to Rp ($Rd/Rp \times 1$ ng)

The estimated detection limits for the target compounds are summarized in Table 3. The total ion current chromatograms of the air particulate extracts analyzed are presented in Appendix A. Since the NCI method cannot provide adequate sensitivity and specificity for all the target compounds, future study with this technique is not recommended.

Analysis of Target Compounds by Positive Chemical Ionization Gas Chromatography/Mass Spectrometry

With the positive chemical ionization (PCI) method, there is very little fragmentation associated with the ionization process. Methane is used as the reagent gas. The most abundant ions in the reaction plasma, CH_5^+ and $C_2H_5^+$, are approximately 90 percent of the ionic content. The ions CH_5^+ and $C_2H_5^+$

TABLE 3. THE ESTIMATED DETECTION LIMITS FOR THE TARGET COMPOUNDS USING GC/MS METHODS

Method	Estimated Detection Limit Range (ng)
EI, Full Scan	10 to 1
EI, SIM	0.1 to 0.001
PCI, Full Scan	10 to 1
PCI, SIM	0.1 to 0.001
NCI, Full Scan	>10 to 0.1
NCI, SIM	1 to 0.001

act as Brönsted acids and protonate the sample molecule. Therefore, the predominant ions formed from the target compounds are protonated molecular ions $(M+H)^+$. Quinoline and isoquinoline contain lone pair electrons, which

are good proton acceptors and can enhance the sensitivity. The estimated detection limit for these compounds is about 0.5 ng on-column in the full scan mode. In the SIM Mode, the mass spectrometer concurrently monitors one or more ion peaks, characteristic of the target compound, during its expected elution time from the gas chromatogram column. Because the ion peaks that are monitored are specific to the target compound being analyzed, ion peaks from other compounds at non-monitored masses will not contribute to the monitored ion current signal. Therefore, other compounds will not interfere with the analysis, and SIM will enhance the sensitivity compared to the full scan mode. In general, the detection limits for the analysis of the target compounds decreased at least 100 times in SIM mode, compared to full scan mode, for EI, PCI, and NCI conditions. While the PCI method does not provide as good sensitivity for analysis of nitropyrene as the NCI method, the PCI method is nevertheless adequately sensitive for this compound (estimated 10 ng on-column in full scan mode and 0.1 ng on-column in SIM mode). The estimated detection limit for the determination of target PAHs ranges from 10 ng to 1 ng on-column by the PCI method in the full scan mode. The detection limits for all the target compounds range from 1-100 pg on-column by PCI GC/MS method in the SIM mode. The estimated detection limits for the determination of target compounds are given in Table 3. Another advantage of using the PCI method is that no clean-up step is required for the determination of target compounds in the air particulate extract. The total sample preparation time and sample cost can thus be significantly decreased. The total ion current chromatograms of the samples analyzed by the PCI method are presented in Appendix A. In conclusion, the PCI method provides adequate detection limits, selectivity, and specificity for the analysis of the target compounds. For this reason, use of the PCI method in the SIM mode is strongly recommended for analysis of the target compounds in the future experimental study.

The identifications of target compounds are based on the correct ion peaks, and the correct relative retention times to the internal standard. Data from the standard analyses showed that the relative retention time for each target compound to the internal standard is very reproducible.

The scan differences between the target compound and the internal standard among different analyses are typically less than 5 scans.

Analysis of Target Compounds by Electron Impact, Gas Chromatography/ Mass Spectrometry

With the electron impact (EI) method, the silica gel clean-up procedure is not required for analyzing the target compounds in air particulate sample matrices. The estimated detection limits for target compounds, using this method, are given in Table 3. The total ion current chromatograms from the EI analysis of the air particulate extracts are presented in Appendix A. The results indicate that the EI method is an appropriate approach for the analysis of the target compounds. The difference between the EI and PCI methods for the determination of the target compounds is that the PCI method provides at least 10 times lower detection limits for quinoline and isoquinoline. Thus, the EI method is not recommended for the future study.

Recovery of Target Compounds from Silica Gel Fractionation

The recoveries of target compounds from the spiked air particulate extract through the silica gel clean-up procedure are given in Table 4. The recovered target compounds were calculated by measuring the difference of the levels of the target compounds between the spiked sample and the non-spiked sample. The data show that the recoveries ranged from 91 to 100 percent for all the target compounds, except for quinoline and isoquinoline, for which the recoveries were less than 10 percent. Losses of quinoline and isoquinoline may occur in the Vortex evaporation step. Another possible explanation for the low recovery of these nitrogen heterocycles is that this type of compound may elute in the methanol fraction. No attempts were made to improve the recovery for these compounds.

ANALYSIS OF TARGET COMPOUNDS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The standards and sample extracts were analyzed by the high performance liquid chromatographic (HPLC) technique, using both ultraviolet and fluorescence detectors. The HPLC system used in this analysis consisted of

TABLE 4. RECOVERY OF TARGET COMPOUNDS IN THE CH_2Cl_2 FRACTION THROUGH THE SILICA GEL CLEAN-UP PROCEDURE

Compound	Percent Recovery
Phenanthrene	100
Fluoranthene	100
Pyrene	100
Cyclopenta(c,d)pyrene	96
Benz(a)anthracene	100
Benzo(e)pyrene	100
Benzo(a)pyrene	99
Benzo(g,h,i)perylene	100
Coronene	100
1-Nitropyrene	91
Quinoline	3
Isoquinoline	7

an Altex Model 430 gradient system with two Model 110A pumps, a Rheodyne variable volume injector with a 10 µL sample injection loop, a Schoeffel FS 970 fluorescence detector, and an LDC Model 1203 UV detector. A reverse phase Altex Ultrasphere ODS 5 micron column was used for this evaluation. In order to improve the resolution of peaks, and to speed up the analysis time, a modified EPA Method 610 (3) solvent system was chosen for the analysis. The HPLC conditions employed are summarized in Table 5.

Analysis of a 13-compound standard mixture (12 target compounds and 1 internal standard for GC/MS analysis) gave 10 peaks using UV detection and 9 peaks using fluorescence detection. Quinoline and isoquinoline standards were not detected under the analytical conditions being used because of their basic properties, that is, quinoline and isoquinoline are ionizable. To obtain satisfactory chromatography for these compounds the mobile phase would require buffering or modifers would need to be added to the mobile phase to prevent these compounds from ionizing. Nitropyrene was measured using UV detection, but not using fluorescence detection. Two of the PAHs in the mixture co-eluted under these chromatographic conditions. Since individual

TABLE 5. HPLC OPERATING CONDITIONS

Column	Altex Ultrasphere -- ODS, 5 micron, 250 x 4.6 nm
Solvent	60% CH_3CN/40% H_2O to 100% CH_3CN, linear, 30 minutes
Flow	1 mL/min
UV Detection	254 nm
Fluorescence Detection	Excitation 280 nm, Emission >370 nm
Injection Volume	10 µL

standards of each of the PAH compounds were not analyzed separately, the two compounds which co-eluted were not identified. No attempts were made to optimize the separation. In conclusion, at least two analyses, including one analysis for nitrogen heterocyclic compounds and one analysis for nitropyrene and PAHs, are required for the determination of all the target compounds by the HPLC method. Estimated detection limits based on analysis of the standards are 1 ng for each compound injected using UV detection, and 100 pg injected using fluorescence detection.

Analysis of the nonfractionated air particulate extract as well as the methylene chloride fraction gave extremely complex chromatograms with numerous peaks. The HPLC chromatograms for these samples are presented in Appendix B. To perform quantitative analysis using the HPLC method on this type of sample matrix, further sample clean-up would be necessary.

COMPARISON OF POSITIVE CHEMICAL IONIZATION GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY METHODS FOR ANALYSIS OF TARGET COMPOUNDS

Both the PCI GC/MS and HPLC methods provide reasonable sensitivity (1 ng to 10 pg) for the determination of the target compounds. As shown in Figure A-4, the total ion chromatogram of the air particulate extract was very

complex, but there were no interference peaks in the extracted ion profiles of the target compounds. It was demonstrated that the PCI GC/MS technique can quantitatively determine the target compounds present in the air particulate extract without the silica gel clean-up procedure. Therefore, all the target compounds can be analyzed in one analysis, and the total analysis time is only 50 minutes. In contrast, in the HPLC technique, organic matter present in the air particulate extract interferes with the detection of the target compounds. A sophisticated fractionation scheme must be developed to remove the UV- and/or fluorescence-sensitive interfering compounds. This step would significantly increase the total sample preparation time. In addition, at least two analysis conditions are required for the determination of all the target compounds in the three compound classes, and this would also increase the total analysis time per sample. A comparison of these two methods is presented in Table 6. Based on this comparison, the PCI GC/MS SIM method is recommended for use in the analysis of PAHs in the experimental study.

TABLE 6. COMPARISON OF ANALYTICAL METHODS

Method	Analyses Per Sample Extract	Total Analysis Time Per Sample, Min	Range for Limit of Quantification, pg	Extract Clean-up Needed	Possibility for Interference	Estimated Cost Per 20 Samples
PCI GC/MS	1	50	50-100	No	No	$20,000(a)
HPLC	≥2	≥60	100-1000	Yes	Yes	$20,000

(a) The estimated cost is for the PCI, GC/MS method in either SIM mode or full can mode.

SECTION 5

DEVELOPMENT OF SAMPLING METHODOLOGY

INTRODUCTION

The objective of this phase of the project was to develop a generic sampling procedure that can be used to collect PAH compounds at various sampling sites. The goal of this development is to categorize the sampling procedures to provide flexibility in selecting the optimum parameters for sample collection, based on a single sampler design. Parameters to be considered are:

- sampler configuration
- sampling time
- sampling temperature
- sampling flow rate
- filter face velocity
- filter capacity for particles
- influence of filter/trap combination on pressure drop
- frequency of sampling
- number of samples to be used
- number of sampling events per site.

If ranges are established for these parameters, the operation of the samplers can be optimized for the site selected.

SAMPLING METHODOLOGY

Several problems in PAH sampling have been identified (1), such as PAH losses and artifact formation during sampling. An acceptable sampler design should minimize these problems and provide representative samples with minimal sample deterioration and contamination. Samples should be collected in sufficient quantity for the level of detection of the analytical method. Quality assurance procedures should be implemented throughout the entire sampling effort, and should treat aspects such as sample handling, sample transport, and sample storage. In addition, the sampler design should

include specific characteristics, such as simplicity of operation, field durability, reliable reproducible operation, convenient size for transport and installation, and compatibility with the sampling environment.

Sampler Configuration

A modified high volume (Hi-Vol) EPA sampler, consisting of a quartz fiber filter to collect particulate matter and a polyurethane foam (PUF) backup trap to collect vapors, is proposed for use in the future experimental study. Both quartz fiber and glass fiber filters are widely used in ambient air sampling, because of their high collection efficiency of at least 99.9 percent for particles 0.3 μm and larger, low resistance to air flow, and low affinity for moisture. A preclean-up procedure is necessary to remove trace amounts of PAHs and interfering compounds from blank glass fiber filters, but this step is not required for the use of quartz fiber filters. Therefore, the use of quartz fiber filters is recommended for the future experimental study. PUF has also demonstrated the ability to trap PAH vapors (4). PUF is easy to handle in the field and has better air flow characteristics than does XAD-2 resin. The use of a PUF backup trap to adsorb vapors can allow correction for filter volatilization losses during sampling. A preliminary study should be conducted, to ensure that the vapors of the target compounds can be quantitatively retained and recovered from the PUF.

No simple scheme to eliminate and/or minimize PAH reactivity losses in sampling has yet been demonstrated. A study involving the design and evaluation of an apparatus for PAH sampling that may eliminate or at least minimize the PAH losses due to ozone and/or NO_2 reactivity is currently being conducted by a Battelle research team. It is recommended that progress on this study be followed and, if possible, incorporated into the proposed sampler design.

Sampling Parameters

The results from the analytical methodology evaluation indicate that about 100 pg of each target compound can be accurately measured by using PCI GC/MS operating in the SIM mode. The volume of air that must be sampled to collect a sufficient quantity of analyte for accurate measurement can then be estimated from the following considerations:

- 0.1 percent of the total sample extract is injected onto the GC column, assuming 1 µL is injected from 1 mL sample extract
- The quantification limit for the analyte using PCI GC/MS is 0.1 ng
- The total amount of analyte required for analysis is 100 ng (0.1 ng 0.1 percent = 100 ng)
- The analyte concentration in ambient air is estimated to be 1 ng/m^3

Therefore, the total air sample volume required is 100 m^3 (100 ng 1 ng/m^3 = 100 m^3). These assumptions require that about 100 m^3 of air be sampled to collect a sufficient amount of PAHs for PCI GC/MS analysis. However, the concentration of PAHs in ambient air can range from 1 ng/m^3 in relatively clean air to over 100 ng/m^3 in polluted air. Thus, the total sample volume required for chemical analysis may vary depending upon the extent of contamination of the sampling sites selected.

Since recent studies indicate that breakthrough of some PAHs from the PUF trap is correlated with air temperature, the sampling temperature should be 20°C or lower. The sampler can be operated at a flow rate of 15-20 m^3/hr. Therefore, an 8-hr sampling time should collect sufficient amounts of sample for analysis. It will be necessary to locate the blower motor unit outside the building because it is very noisy when the motor is operating. A flexible hose can be used to connect the motor unit and the dual chamber sampling module. The dual sampling module can then be located entirely inside the building sampling site.

The filter capacity for particles will depend upon the type of microenvironment sampled. A preliminary study should be conducted to determine this capacity, and to evaluate the influence of filter/trap combination on pressure drop. This study can be carried out by sampling two extreme microenvironments, one relatively clean and one highly polluted environment. The number of samplers to be used and the number of sampling events per site will depend on the individual study design. For the future range-finding study, these parameters are detailed in Section 7 (Design of a Pilot Study). Based on the results of the pilot study, these parameters may then be established for the future experimental study. The estimated

sampling parameters for the microenvironment sampling procedure are summarized in Table 7.

TABLE 7. PARAMETERS FOR A GENERIC SAMPLING PROCEDURE FOR AIR IN MICROENVIRONMENTS

Sampling Parameter	Conditions
Sampling Volume	100 m^3
Sampling Time	8 hr
Sampling Temperature	$\leq 20^{o}C$
Sampling Flow Rate	15-20 m^3/hr
Filter Face Velocity	30-40 m/min(a)
Filter Capacity for Particles	Very high
Frequency of Sampling	--(b)
Number of Sampling Events per Site	--(b)
Number of PUF Traps	One

(a) Filter face velocity is calculated from the sampling flow rate at sampling temperature/pressure conditions, divided by the filter exposure area.

(b) These parameters will depend on the particular study design.

SECTION 6

THE INFLUENCE OF CIGARETTE SMOKE ON THE POLYNUCLEAR AROMATIC COMPOUND CONCENTRATION IN AIR IN MICROENVIRONMENTS

INTRODUCTION

Cigarette smoke may contribute significantly to the levels of PAHs in air, particularly within microenvironments such as residences or work places. Quinoline and isoquinoline have been suggested by several research groups as possible marker compounds that might indicate the level of cigarette smoke. To determine the contribution of cigarette smoke to the total PAH concentration in air and to establish the extent to which the PAH concentration resulting from cigarette smoke can be inferred based on the measurement of quinoline and isoquinoline, a brief literature survey was conducted. Over 100 citations were obtained as a result of a computer search of eight data bases including Chemical Abstracts, APTIC, NTIS, Environline, Pollution Abstracts, BIOSIS, Excerpta Media, and Med Line, covering the years 1964-1983. These citations were reviewed and those that were most relevant to the subject area were selected for detailed evaluation.

PAH PROFILES* IN CIGARETTE SMOKE

The results of this survey indicate that hundreds of PAHs and their derivatives, including all of the target compounds except nitropyrene have been detected in cigarette smoke condensate (CSC). Higher levels of methylated PAHs have been found in CSC relative to other emission sources, such as diesel exhaust or coal combustion emissions (5-8,10,13,11,14). Considerable information (5-18) is available on the levels of PAHs in CSC in

---

* The term profile, in this report, represents the PAH concentration in the cigarette smoke condensate (μg/cigarette) or in air (μg/m^3).

terms of µg of PAHs per cigarette, but only a few studies (19,20) have determined the PAH concentrations in air (µg/m^3) within microenvironments that result from cigarette smoking. Comparison of the levels of PAHs from cigarette smoke between these two categories is complicated, because of the difficulty in calculating the dilution factor between PAHs in CSC and PAHs in air.

One generalization resulting from this survey is that the concentrations of individual PAH in CSC varies from about 1 ng/cigarette to more than 1000 ng/cigarette. This variation may be due to the effects of the filter, tobacco types, tobacco processing methods, and chemical additives on the cigarette. One study (14) showed that filters on cigarettes not only reduced the amount of CSC, but also selectively decreased the levels of PAHs in CSC. Both of the commercially used cellulose acetate and charcoal-cellulose acetate filters can reduce the levels of certain PAHs in the CSC to less than 50 percent of the levels produced by unfiltered cigarettes.

Savino and coworkers (16) showed that the benzo(a)pyrene (BaP) concentration in the side stream smoke of a cigarette, produced by glowing between the puffs, was more than 2.5 times that present in the main stream smoke, inhaled by the smoker. These authors also pointed out that the quantities of tar and nicotine in the side stream smoke were greater than those present in the main stream smoke, except for the nicotine in the nonfiltered cigarettes. Grimmer's group (19) observed the same comparative concentrations, and showed that the ratio of the PAH concentration in terms of ng/m^3 in the side stream and the main stream smoke was different among PAH compounds and ranged from 1.8 to 6.4. This study shows the importance of evaluating the composition of cigarette smoke dispersed in room air and of assessing the danger to which non-smokers are exposed in rooms where other people are smoking.

Grimmer's group conducted a study (19) to measure the PAH concentrations in air within a room that had a machine smoking cigarettes. The smoking machine was operated under standard conditions of puff frequency (1/min), puff time (2 sec), puff volume (35 mL) and butt length (23 mm). The results indicated that the levels of PAHs produced by cigarette smoking were independent of the season. For example, the concentration of benzo(a)pyrene

(BaP) produced by smoking a single test cigarette was in the range of 9.7 to 11.1 ng/m^3 on different testing dates (March 15 and September 4, 1975). In contrast, the concentration of BaP in the ambient air was dependent on the season, for example, 5 ng/m^3 on September 4, 1975 and 68 ng/m^3 on March 15, 1975. The same research group performed another study (20) to investigate the relationship between the levels of 16 selected PAHs and cigarette smoking in air within a microenvironment in which a smoking machine was operated at standard conditions. Filtered air was sampled in a 30 m^3 test room with an air exchange rate of 36 m^3/hr. During the 8-hour sampling period, five cigarettes per hour were smoked by the machine. On four successive days, the average concentration of BaP in this room air was 22 ng/m^3. These BaP concentrations are at least 10-fold higher than that in typically clean ambient air. It is very likely that cigarette smoking is a major contributor to the PAH contamination in air within residences and work places.

QUINOLINE AND ISOQUINOLINE CONCENTRATIONS IN CIGARETTE SMOKE CONDENSATE

Only a few studies available in this survey indicated that quinoline and isoquinoline were present in cigarette smoke (21-24). One study (21) showed that the level of quinoline was approximately equivalent to the naphthalene level in CSC, but it was about 70 times greater than that of BaP in CSC from the same type of cigarette. The same research group (23) showed that quinoline was the most abundant aza-arene compound in the smoke, and was present at levels about 11 times greater in the side stream smoke than in the main stream smoke. The authors suggested that tobacco leaf proteins are major precursors for quinoline in cigarette smoke and showed that selective reduction of quinoline levels can be achieved by the use of tobacco of low protein content. It should also be noted that these types of compounds were major components from coal combustion emission (25-28), and were also found in ambient air particulate matter (29,30) and automobile exhaust (31). For these reasons, it may not be feasible to use quinoline and isoquinoline as marker compounds as evidence of the level of cigarette smoke within microenvironments.

SECTION 7

DESIGN OF A PILOT STUDY

INTRODUCTION

A study will be conducted in Columbus, Ohio during the winter of 1983-1984 to determine the PAH concentration in air. The purpose of the study is to gather background information for use in developing a design for a larger scale study to be conducted in 1985. The specific objectives of the pilot study are to:

(a) Estimate the ranges of PAH levels in various microenvironments of interest,

(b) Identify factors that systematically contribute to the PAH levels observed,

(c) Obtain rough estimates of the relative magnitudes of the different sources of variation,

(d) Refine the sampling methodology and protocols,

(e) Identify practical limitations on the sampling equipment and methodology, and

(f) Obtain better information concerning the actual costs associated with the sampling of PAHs.

Very few field sampling studies have been conducted for PAHs and therefore little is known concerning the problems and issues involved in the implementation of such a study. By addressing each of the objectives just cited, the pilot study will provide the necessary information for designing a larger field study.

SELECTION OF SAMPLE RESIDENCES

Battelle and EPA have decided that it is appropriate for the pilot study to address PAH levels only in residences. The study of other types of

microenvironments, while useful, would greatly increase the required time and cost of the study. It was thought that a study of residences can provide the necessary information for designing a sound, comprehensive, full scale study.

For the pilot study, there are a number of factors expected to have significant effects on the levels of PAHs observed. The three primary factors are: the presence or absence of cigarette smokers, the use or non-use of a wood burning fireplace, and the presence or absence of gas appliances and heating system. Since these are considered to be the most important factors, they have been incorporated into the experimental design. This ensures that residences that have specific characteristics with respect to these factors are included in the study.

The study will involve sampling PAH levels at nine different residences. One of the residences will be used as a control and the remaining eight will be selected according to specific characteristics. The types of residences that will be selected are as follows:

(a) One Control Home

- all electric appliances and heating system
- no cigarette smokers present
- no wood burning fireplace in use during the survey.

(b) Eight Experimental Homes

- all gas appliances and heating system
- various combinations of conditions with respect to cigarette smoking and wood burning fireplaces.

The specific design for the experimental homes is given in Figure 2.

The use of a specific experimental design for selecting the study homes allows a systematic evaluation to be performed concerning the effects of each of the critical factors on the PAH levels. Such a design provides for estimates to be made of the individual contribution of each factor. Since only two homes of each type are being studied, the estimates will not be very precise. However, order-of-magnitude differences among the factors will be detectable. This is the type of information required from the pilot study to determine the proper sample allocations for the full scale study.

		Cigarette Smoking	
		Absent	Present
Wood Burning Fireplace	Not In Use	Home 1 Home 2	Home 5 Home 6
	In Use	Home 3 Home 4	Home 7 Home 8

Figure 2. Design for selection of the experimental homes.

For example, if the presence or absence of cigarette smokers is found to be not as important as other factors, smoking will play a less important role in the design of a full scale study. If there is considerable variation in PAH levels among homes within the same categories, a larger number of homes will need to be surveyed in the full scale field study in order to precisely estimate the effects of the experimental factors.

SAMPLING PERIODS AND LOCATIONS

Each of the residence surveys will be conducted over 24 hours. The sampling will be divided into three 8-hour periods, with different locations within the residence monitored during each period. The following scheme will be used:

(a) 3:00 p.m. -- 11:00 p.m. (Living Area)
(b) 11:00 p.m. -- 7:00 a.m. (Bedroom)
(c) 7:00 a.m. -- 3:00 p.m. (Kitchen).

Based on a preliminary evaluation of the sensitivity of the analytical procedures and the expected PAH concentrations, 8-hour sampling periods should provide for collection of sufficient amounts of PAH for precise analytical determinations. The use of different sampling locations will provide for estimates to be made of variations of PAH levels throughout the different locations within the home. The choice of times and locations correspond to those in which the residents spend the majority of their time.

At the same time that the interior locations of the residence are being monitored, background levels outside the residence will also be monitored. These measurements will provide for comparisons between interior PAH levels and background levels. A single background measurement will be taken over the entire 24-hour sampling period. To help establish relationships between interior and exterior levels, measurements of the air exchange rates for the residence will be obtained during all surveys. The air exchange rate measurements will also provide valuable information concerning variations in interior PAH levels that are not explained by the design factors--gas/electric appliances, smoking, and fireplaces. It is expected that homes that are less airtight will generally have lower PAH levels than would airtight homes under the same experimental conditions.

To obtain estimates of day-to-day variations of PAH levels within residences, several of the experimental residences will be surveyed on a second day. The residences that will be surveyed on a second day are:

(a) One home having no smokers and no wood burning fireplace in use

(b) One home having smokers and having a wood burning fireplace in use.

This covers the two extremes among the experimental homes, and will provide information concerning the magnitude of day-to-day variations at different PAH levels. If day-to-day variations are found to be large relative to other factors, the full scale study will need to include more survey days per home in order to precisely estimate a home's typical PAH level. An overview of the entire survey design is presented in Figure 3.

DATA TO BE COLLECTED

Several types of information will be collected during the survey of a residence. This information includes:

(a) Identification information concerning the date, time and location of the survey; the sampling instrumentation used; and the personnel involved.

(b) Measurement data concerning the PAH levels observed, including QA/QC data obtained from the analysis lab.

(c) Time of the 8-hour sampling periods and the locations monitored.

(d) Background PAH levels measured for the entire 24-hour period.

(e) Air exchange rate measurements.

(f) Demographic information concerning the residents of the home, and structural characteristics of the home.

(g) Activities conducted in the home during the survey.

(h) Meteorological data, e.g., wind direction, wind speed, and temperature.

The ancillary information collected will be used to help interpret the PAH measurements observed, and to identify other possible factors that have significant influences on the levels. For example, activities such as vacuum cleaning during the sample period could increase the levels of airborne particles carrying PAHs, and thus result in higher observed PAH levels.

Questionnaires and other data forms will be developed to record the information desired. Their use during the range-finding study will indicate areas where data form improvements are needed. Data handling and processing procedures will also be refined during the study. QA/QC activities that will provide for better quality data and fewer data losses during the full scale field study will be identified.

Control Homes
All Electric Appliances
Electric Heating System

	Smokers Absent
Fireplace Not In Use	Home 1 Home 2

Experimental Homes
All Gas Appliances
Gas Heating System

		Smokers	
		Absent	Present
Fireplace	Not In Use	Home 3(a) Home 4	Home 7 Home 8
	In Use	Home 5 Home 6	Home 9(a) Home 10

(a) Indicates that the home will be surveyed on two different days.

Figure 3. Overview of the experimental design for the pilot study.

REFERENCES

(1) Chuang, C. C. and Petersen, B. A., "Review of Sampling and Analytical Methodology for Polynuclear Aromatic Compounds in Air from Mobile Sources", Project Report, U.S. EPA, Contract 68-02-3169, 1984.

(2) Petersen, B. A. and Chuang, C. C., "Methodology of Fractionation and Partition of Diesel Exhaust Particulate Samples", Toxicological Effects of Emissions from Diesel Engines, 10, 51-67 (1982), edited by J. Lewtas, New York, Elselvier Biomedical Press.

(3) Longbottom, J. E. and Lichtenberg, J. J., Editors, "Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater: Method 610 Polynuclear Aromatic Hydrocarbons", EPA-600/4-82-057, July 1982.

(4) Keller, C. D., and Bidleman, T. F., "Collection of Airborne Polycyclic Aromatic Hydrocarbons and Other Organics with a Glass Fiber Filter Polyurethane Foam System", Atmos. Environ., 18:837-845, 1984.

(5) Hecht, S. S., Bondinell, W. E. and Hoffmann, D., "Chrysene and Methylchrysenes: Presence in Tobacco Smoke and Carcinogenicity", J. Natl. Cancer Inst. (U.S.A.), 53, 1121-1133 (1974).

(6) Brunnemann, K. D. and Hoffmann, D., "Analysis of Polynuclear Aromatic Hydrocarbons in the Respiratory Environment", Carcinogenesis, 1, 283-297 (1976), edited by P. W. Jones and R. I. Freudenthal, New York, Raven Press.

(7) Hoffmann, D., Bondinell, W. E. and Wynder, C. L., "Carcinogenicity of Methylchrysene", Science, 183, 215-216 (1974).

(8) Snook, M. E., Severson, R. F., Arrendale, R. F., Higman, H. C. and Chortyk, O. T., "Multi Alkylated Polynuclear Aromatic Hydrocarbons of Tobacco Smoke Separation and Identification", Beitr. Tabakforsch, 9(4), 222-247 (1978).

(9) Scassellati-Sforzolini, G., "Tobacco Smoke in an Enclosed Space", Il Fumo di Tabacco Negli Ambienti Confinati. Fumi Polveri (Milan), 7, 38-41 (1967).

(10) Stedman, R. L., "The Chemical Composition of Tobacco and Tobacco Smoke", Chem. Rev., 68(2), 153-207 (1968).

(11) Gilbert, J. A. S. and Lindsey, A. J., "Polycyclic Hydrocarbons in Tobacco Smoke: Pipe Smoking Experiments", Brit. J. Cancer (London), 10, 646-648 (1956).

(12) Akin, F. J., Snook, M. E., Severson, R. E., Chamberlain, W. J. and Walters, D. B., "Identification of Polynuclear Aromatic Hydrocarbons in Cigarette Smoke and Their Importance as Tumorigens", J. Natl. Cancer Inst., 57(1), 191-195 (1976).

(13) Severson, R. F., Snook, M. E., Higman, H. C., Chortyk, O. T. and Akin, F. J., "Isolation, Identification, and Quantitation of the Polynuclear Aromatic Hydrocarbons in Tobacco Smoke", Carcinogenesis, 1, 253-270 (1976), edited by P. W. Jones and R. I. Freudenthal, New York, Raven Press.

(14) Severson, R. F., Snook, M. E., Arrendale, R. F. and Chortyk, O. T., "Gas Chromatographic Quantitation of Polynuclear Aromatic Hydrocarbons in Tobacco Smoke", Anal. Chem., 48, 1866-1872 (1976).

(15) Snook, M. E., Severson, R. F., Arrendale, R. F., Higman, H. C. and Chortyk, O. T., "The Identification of High Molecular Weight Polynuclear Aromatic Hydrocarbons in a Biologically Active Fraction of Cigarette Smoke Condensate", Beitr. Tabakforsch, 9(2), 79-101 (1977).

(16) Scassellati-Sforzolini, G. and Savino, A., "Evaluation of a Rapid Index of Environmental Pollution by Tobacco Smoke and Study of the Composition of the Main-stream and Side-stream Cigarette Smoke", EUR 5360, Proc. Int. Symp. Recent Adv. Assess-Health Eff. Environ. Pollut., 3, 1749-1756 (Eng) (1975).

(17) Haeberer, A. F., Snook, M. E. and Chortyk, O. T., "High-pressure Liquid Chromatography of Polynuclear Aromatic Hydrocarbons of Cigarette Smoke Condensate", Anal. Chem. Acta, 80(2), 303-309 (1975).

(18) Briggs, C. D. and Hawthorne, S. J. A., "Determination of Polycyclic Aromatic Hydrocarbons in Tobacco Smoke Condensate", Proc. Anal. Div. Chem. Soc., 15(6), 181-184 (1978).

(19) Grimmer, G., Boehnke, H. and Harke, H. P., "Passive Smoking Measuring of Concentrations of Polycyclic Aromatic Hydrocarbons in Rooms After Machine Smoking of Cigarettes", Int. Arch. Occup. Environ. Health, 40(2), 83-92 (1977).

(20) Grimmer, G., Boehnke, H. and Harke, H. P., "Passive Smoking Intake of Polycyclic Aromatic Hydrocarbons by Breathing of Cigarette Smoke Containing Air", Int. Arch. Occup. Environ. Health, 40, 93-100 (1977).

(21) Dong, M., Schmeltz, I., LaVoie, E. and Hoffmann, D., "Aza-Arenes in the Respiratory Environment: Analysis and Assays for Mutagenicity", Carcinogensis, 3, 97-108 (1978), edited by P. W. Jones and R. I. Freudenthal, Raven Press, New York.

(22) Snook, M. E., Fortson, P. J. and Chortyk, O. T., "Isolation and Identification of Aza-Arenes of Tobacco Smoke", Beitr. Tabakforsch, 11(3), 67-78 (1981).

(23) Dong, M., Schmeltz, I., Jacobs, E. and Hoffmann, D., "Aza Arenes in Tobacco Smoke", J. Anal. Toxicol., 2(1), 21-25 (1978).

(24) Klus, H. and Kuhn, H., "Contribution to the Information on Weakly Basic and Weakly Acidic Polycyclic Aromatic Hydrocarbons in Tobacco Smoke. Part I. (A.) Methods and Preliminary Tests. (B.) Quinoline and Acridine Fractions", Fachliche Mitt. Oesterr. Tabakregie, 17, 348-368 (1977).

(25) Sawicki, E., Stanley, T. W. and Elbert, W. C., "The Application of Thin-Layer Chromatographic and Spectral Procedures to the Analysis for Aza Heterocyclic Hydrocarbons in Complex Mixtures", Occupational Health Rev., 16(3), 8-16 (1964).

(26) Buonicore, A. J., "Analyzing Organics in Air Emissions", Environ. Sci. & Tech., 13(11), 1340-1342 (1979).

(27) Berstroem, J. G. T., Eklund, G. and Trzciniski, K., "Characterization and Comparison of Organic Emissions from Coal-, Oil- and Wood-fired Boilers", Polynuclear Aromatic Hydrocarbons: Phys. Biol. Chem., Int. Symp., 6th Editors: Cooke, W. M., Dennis, A. J., and Fisher, G. L., 109-120 (1982).

(28) Ortuglio, C., Walters, J. G. and Wolfson, D. E., "Coal Carbonization Studies: Altering Composition and Yield of Volatile Products by Increasing the Free Space Above the Charge", Bureau of Mines, Washington, D. C., Report No. RI-7400, 15 (1970).

(29) Dong, M. W., Locke, D. C. and Hoffmann, D., "Characterization of Aza-Arenes in Basic Organic Portion of Suspended Particulate Matter", Environ Sci. & Tech., 11(6), 612 (1977).

(30) Adams, J., Atlas, E. L. and Giam, C. S., "Ultratrace Determination of Vapor-Phase Nitrogen Heterocyclic Bases in Ambient Air", Anal. Chem., 54(9), 1515-1518 (1982).

(31) Sawicki, E., Meeker, J. E. and Morgan, M., "Polynuclear Aza Compounds in Automotive Exhaust", Arch. Environ. Health, 11, 773-775 (1965).

APPENDIX A

TOTAL ION CURRENT CHROMATOGRAMS FROM NCI, PCI, AND EI GC/MS ANALYSIS OF THE AIR PARTICULATE EXTRACT SAMPLES

TABLE A-1. TARGET COMPOUNDS IDENTIFIED IN THE STANDARD SOLUTIONS AND THE SAMPLE EXTRACTS

Peak Number	Compound Name
1	Quinoline
2	Isoquinoline
3	Phenanthrene
4	Fluoranthene
5	Pyrene
6	Cyclopenta(c,d)pyrene
7	Benz(a)anthracene
8	1-nitropyrene
9	Benzo(e)pyrene
10	Benzo(a)pyrene
11	Benzo(g,h,i)perylene
12	Coronene

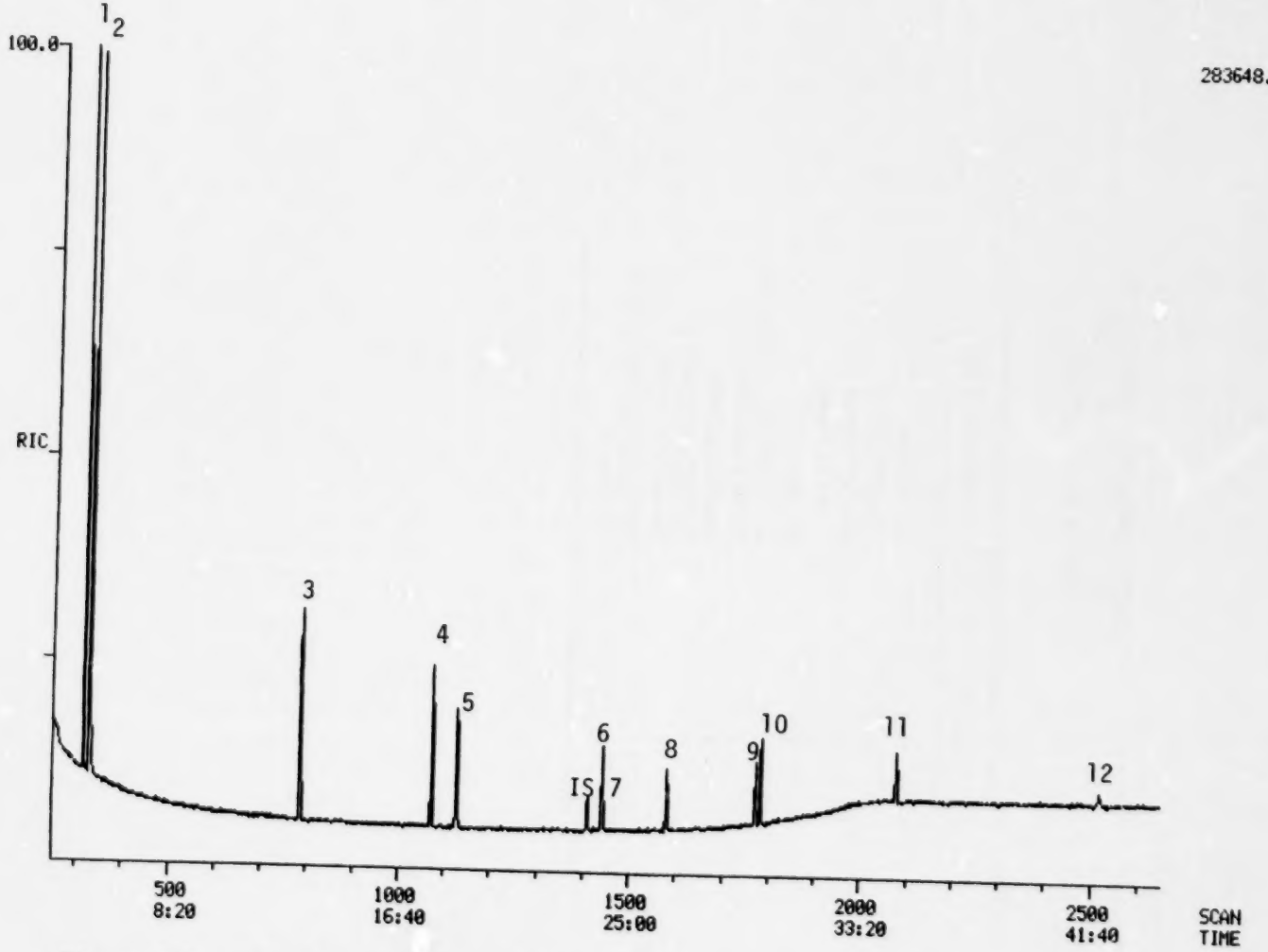

Figure A-1. Total ion current and selected ion current chromatograms from PCI GC/MS analysis of the target compound standard solution.

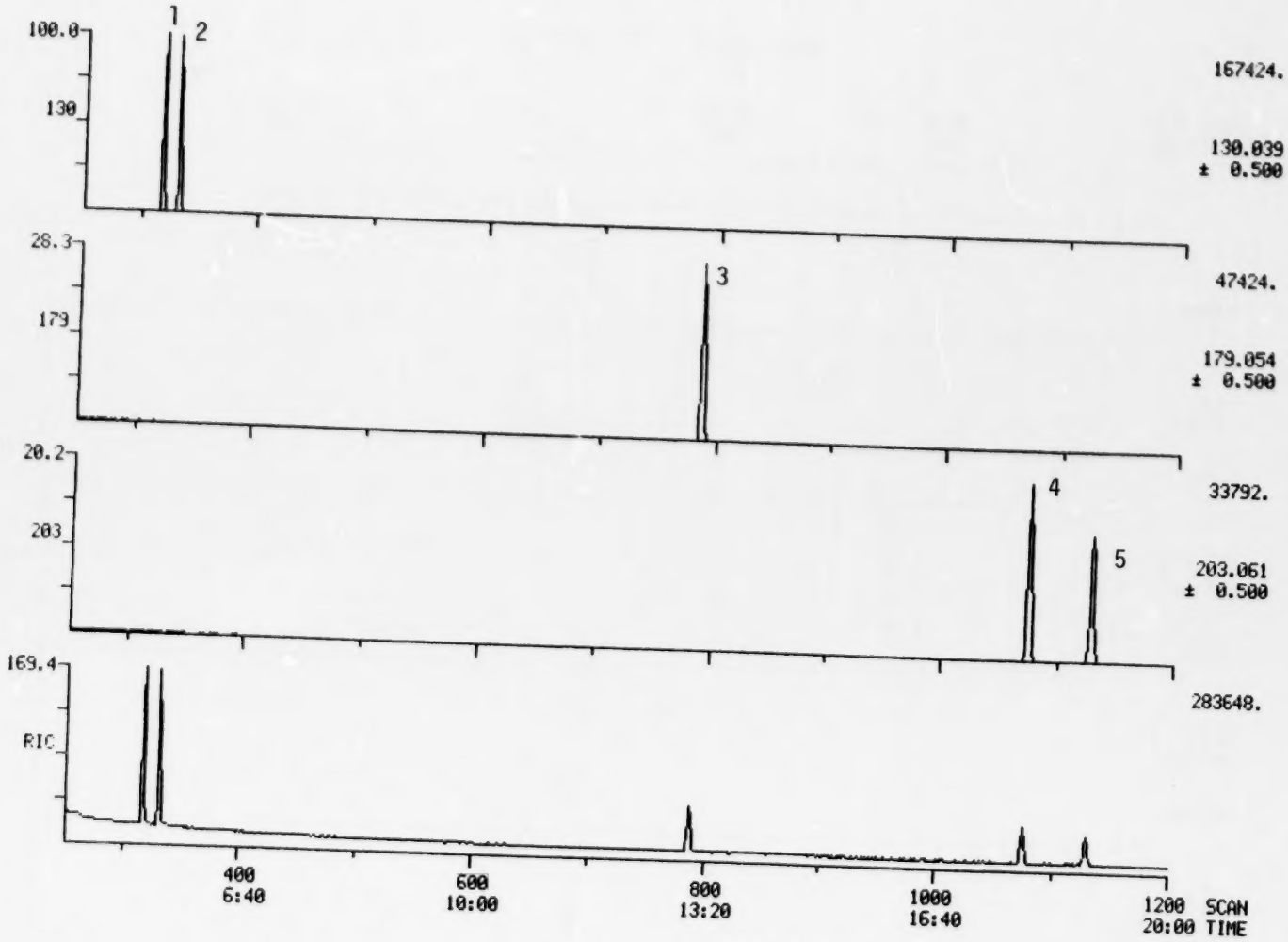

Figure A-1. (Continued)

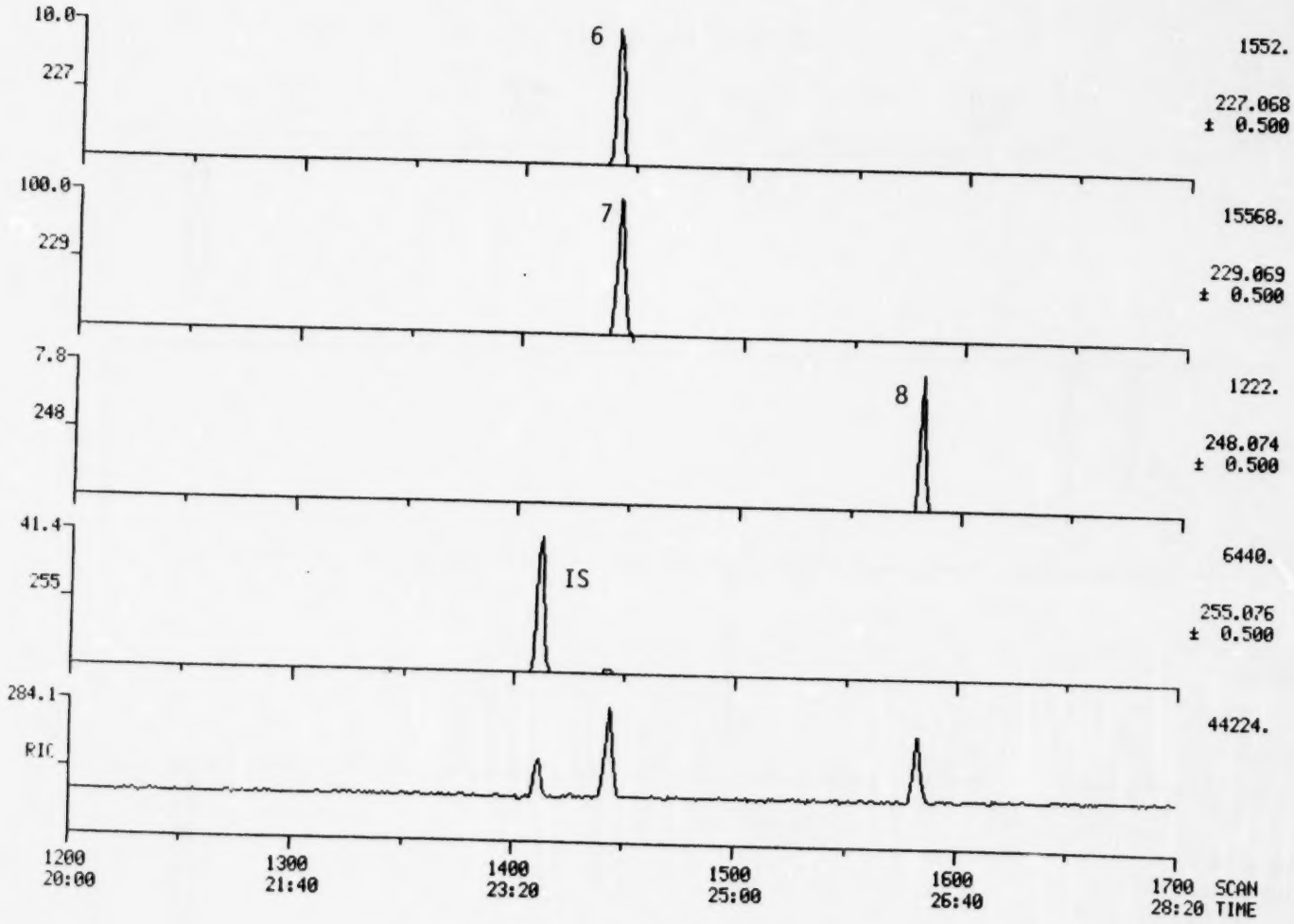

Figure A-1. (Continued)

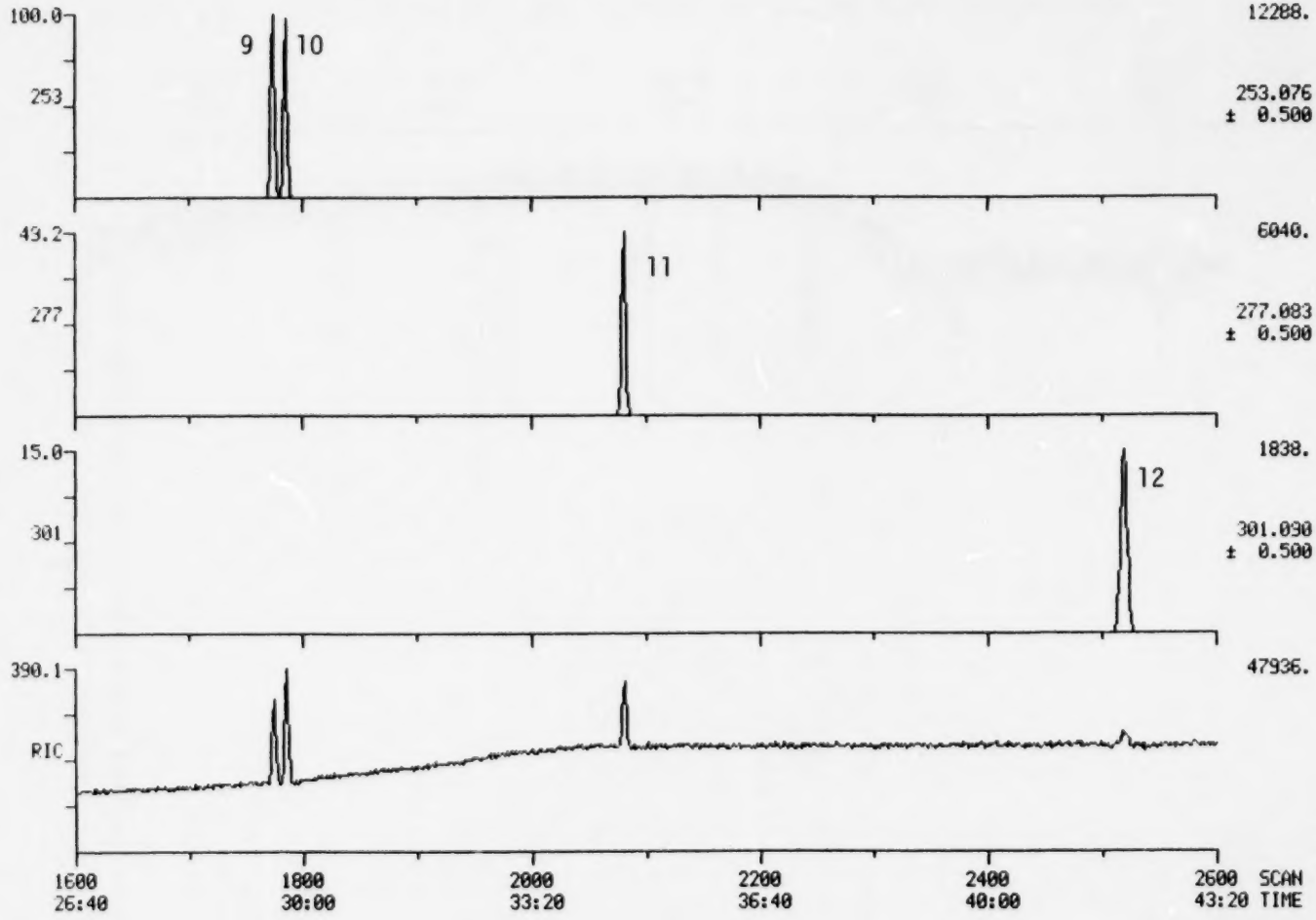

Figure A-1. (Continued)

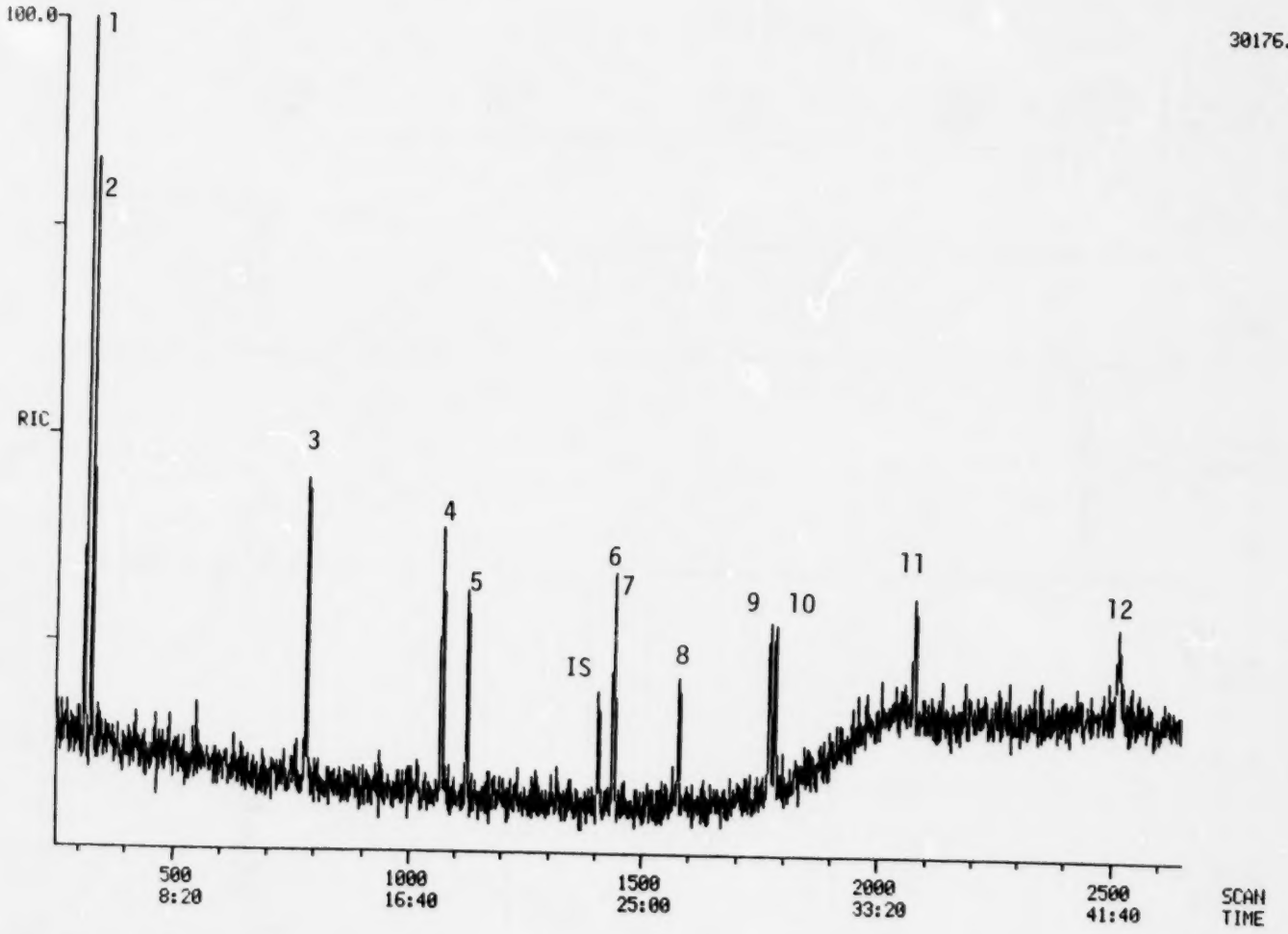

Figure A-2. Total ion current and selected ion current chromatograms from EI GC/MS analysis of the target compound standard solution.

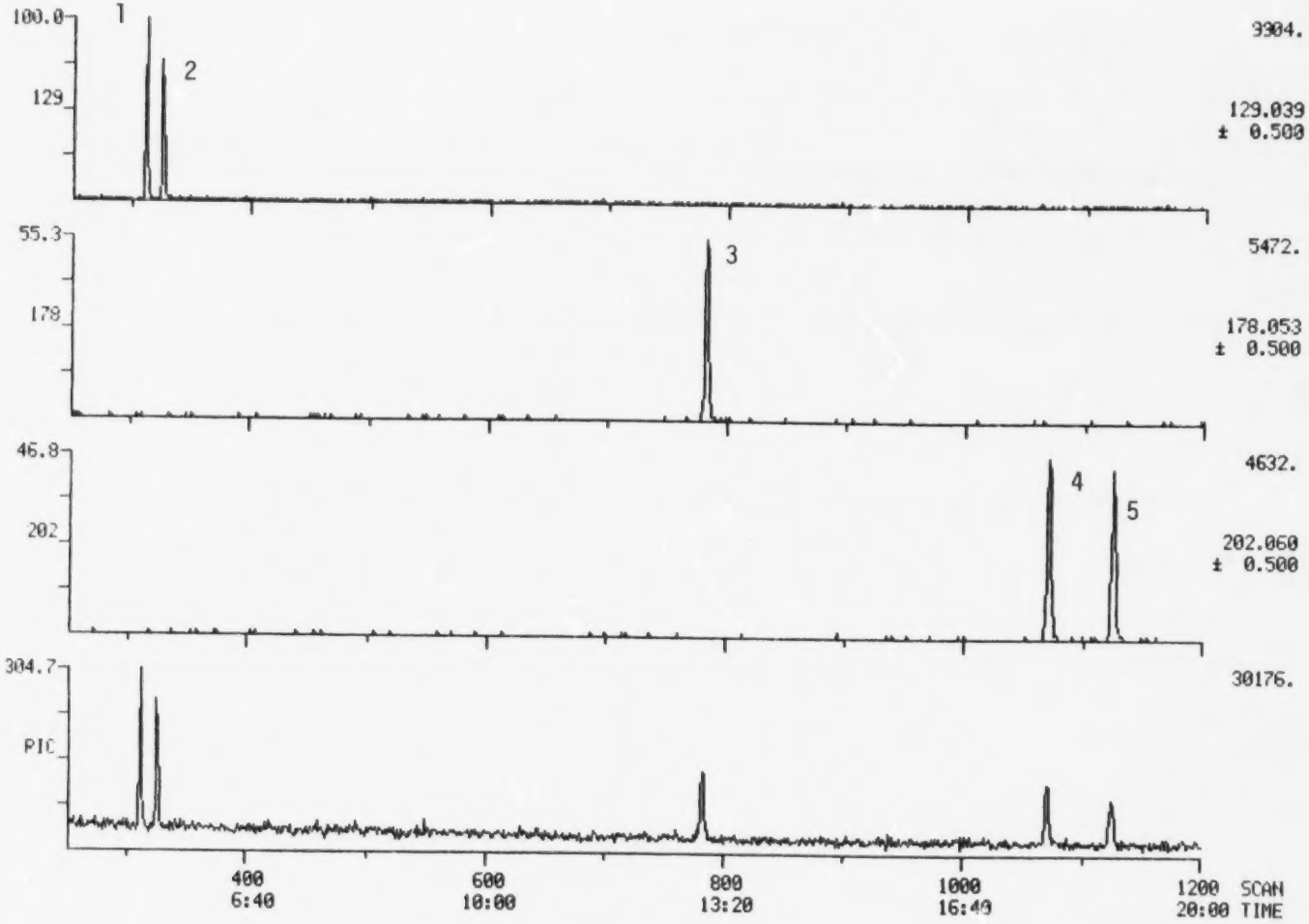

Figure A-2. (Continued)

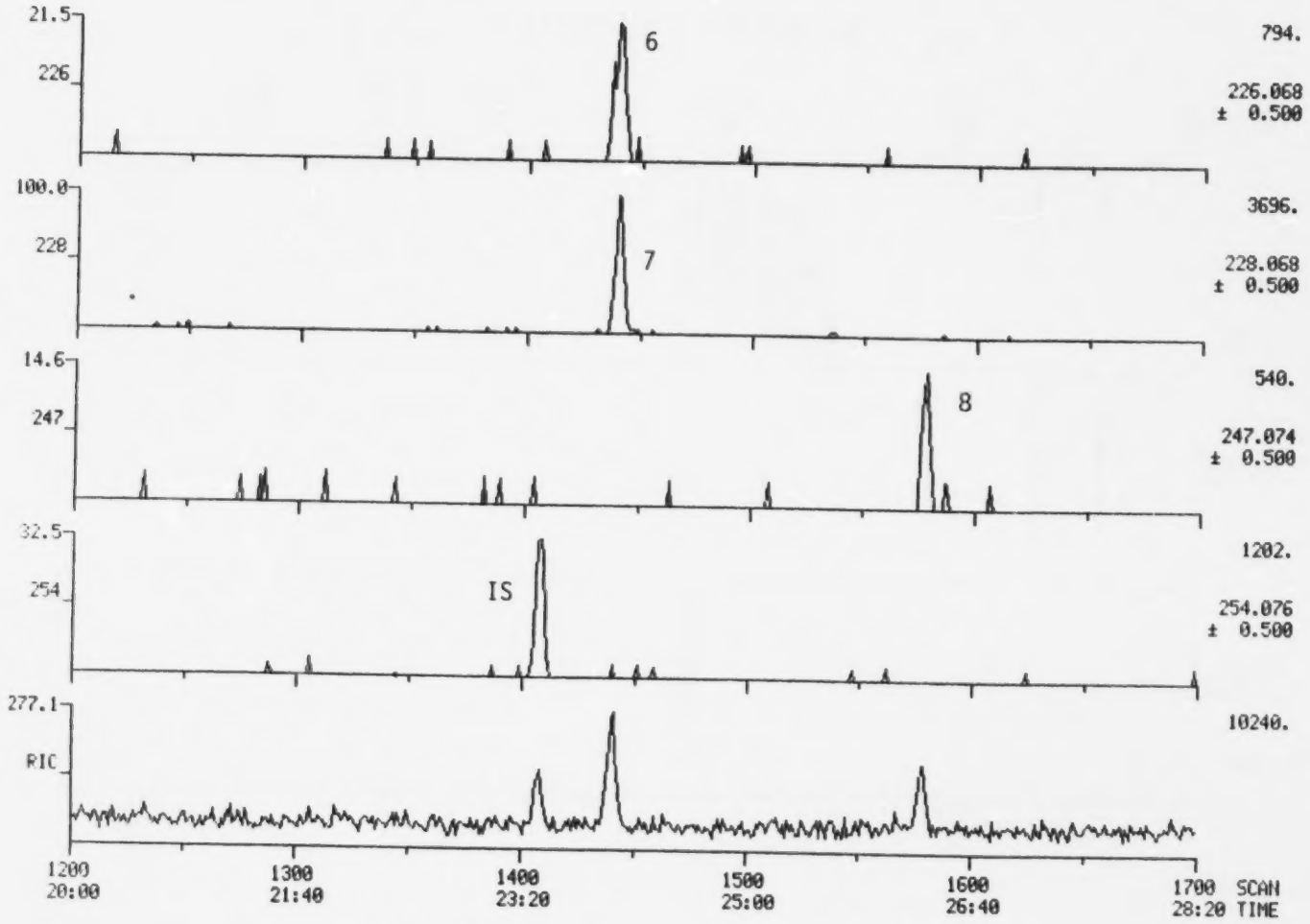

Figure A-2. (Continued)

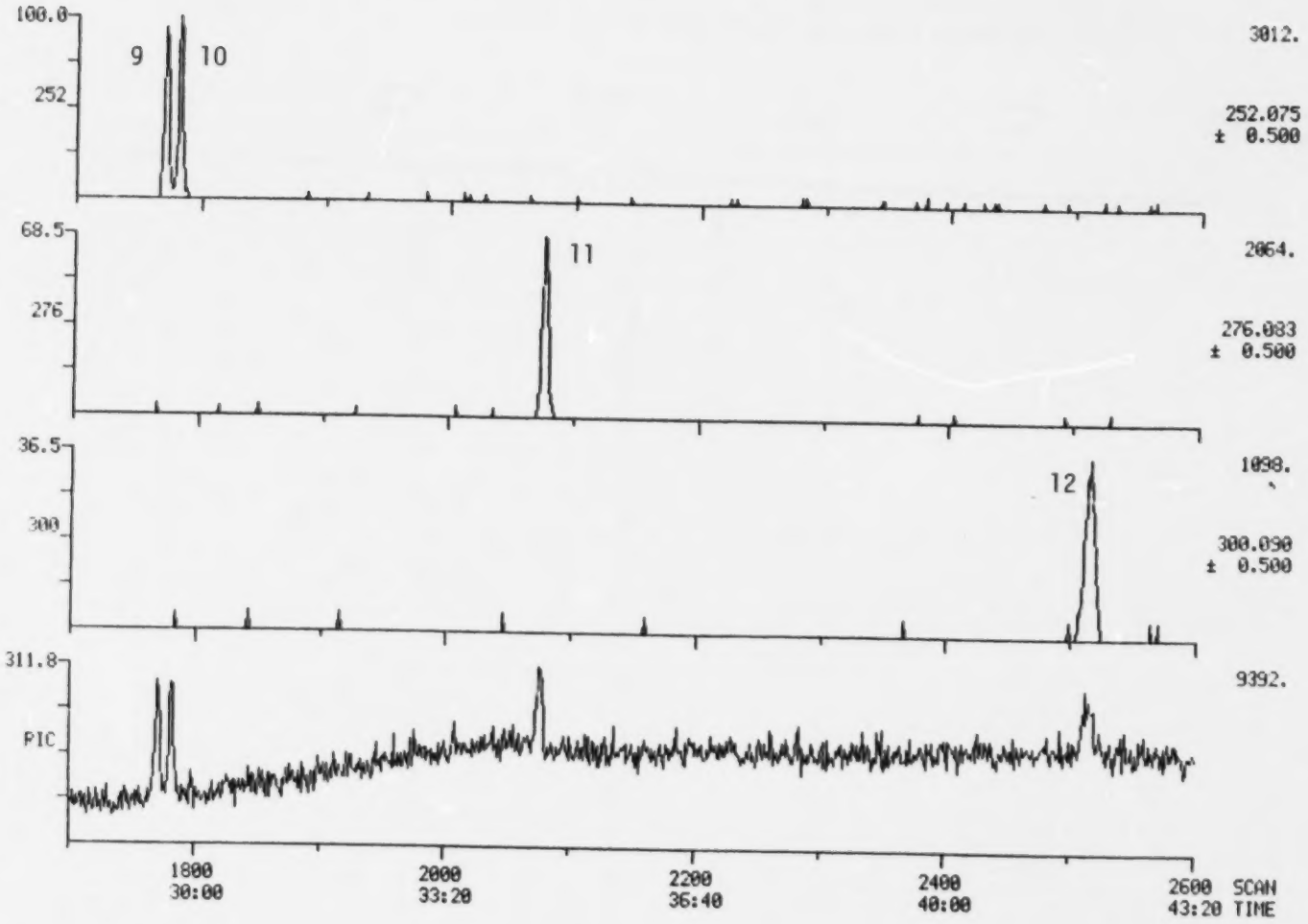

Figure A-2. (Continued)

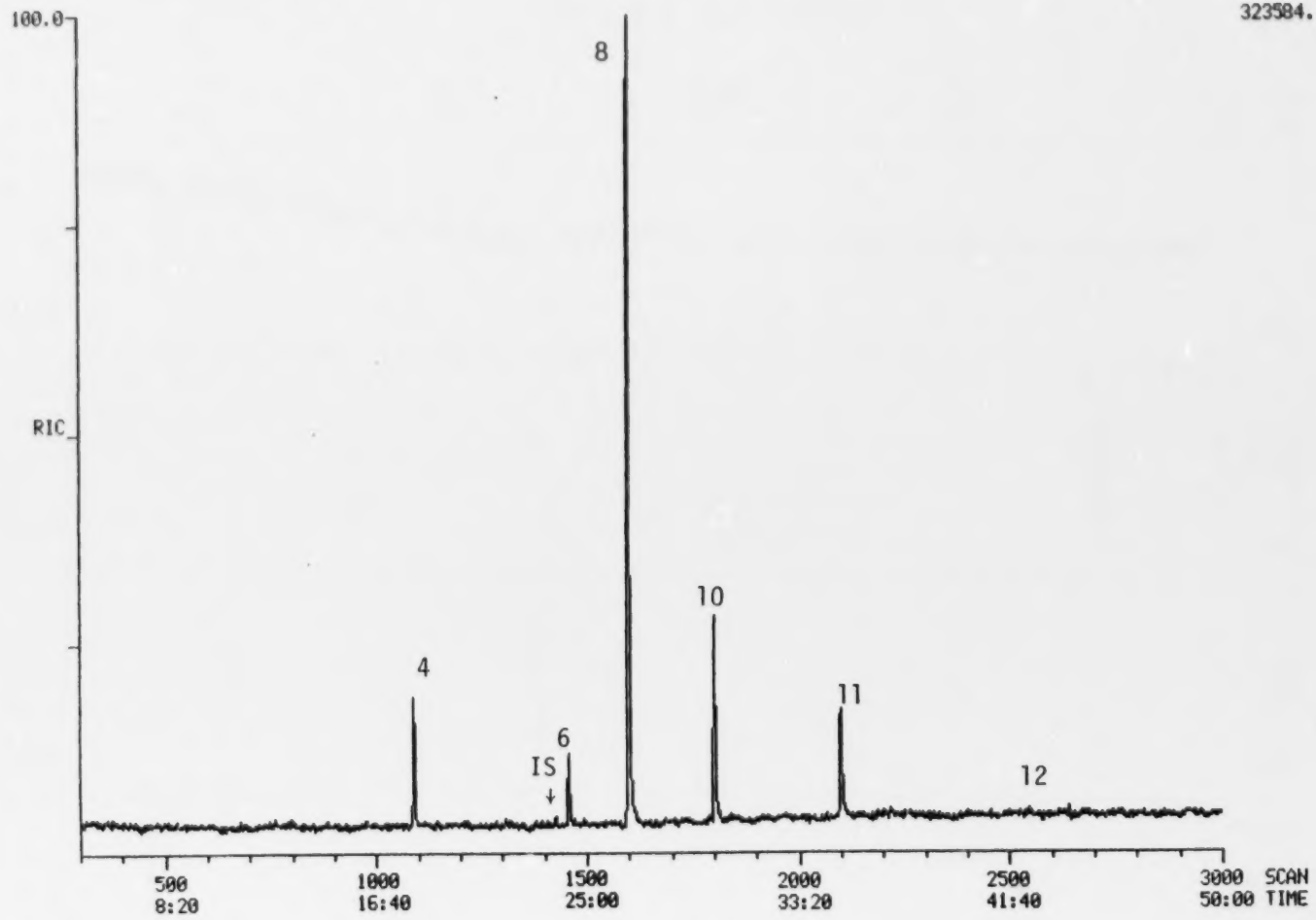

Figure A-3. Total ion current and selected ion current chromatograms from NCI GC/MS analysis of the target compound standard solution.

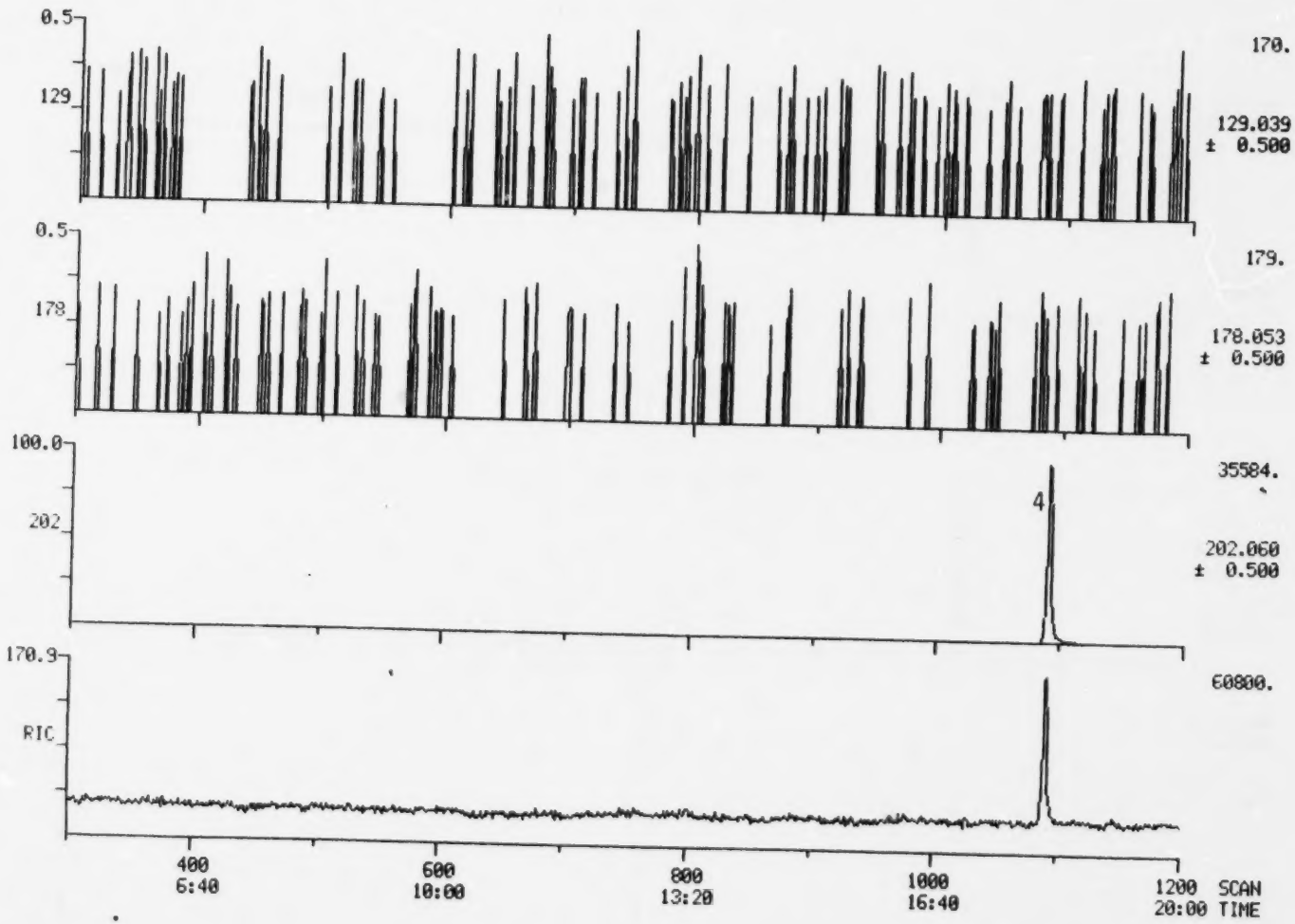

Figure A-3. (Continued)

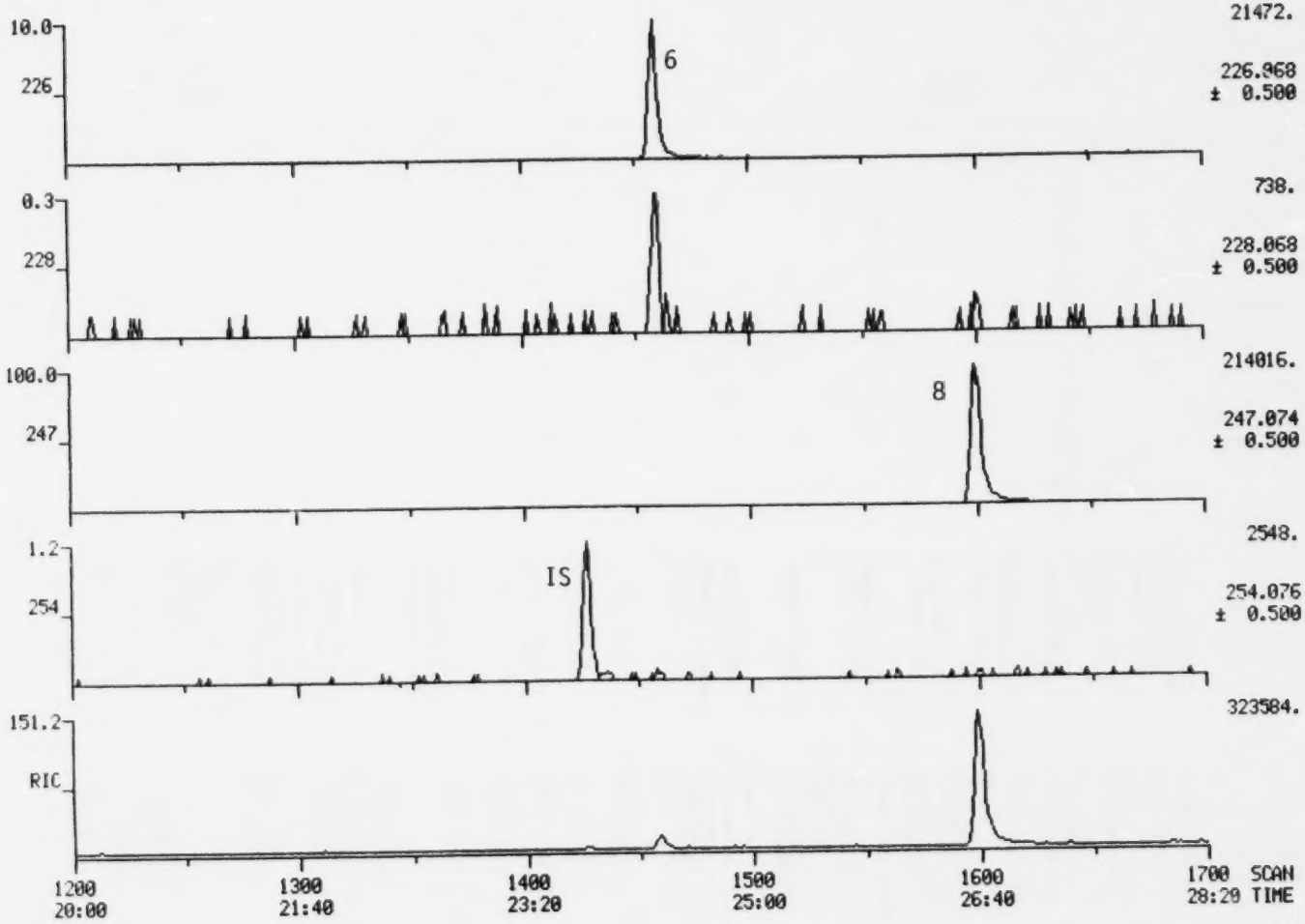

Figure A-3. (Continued)

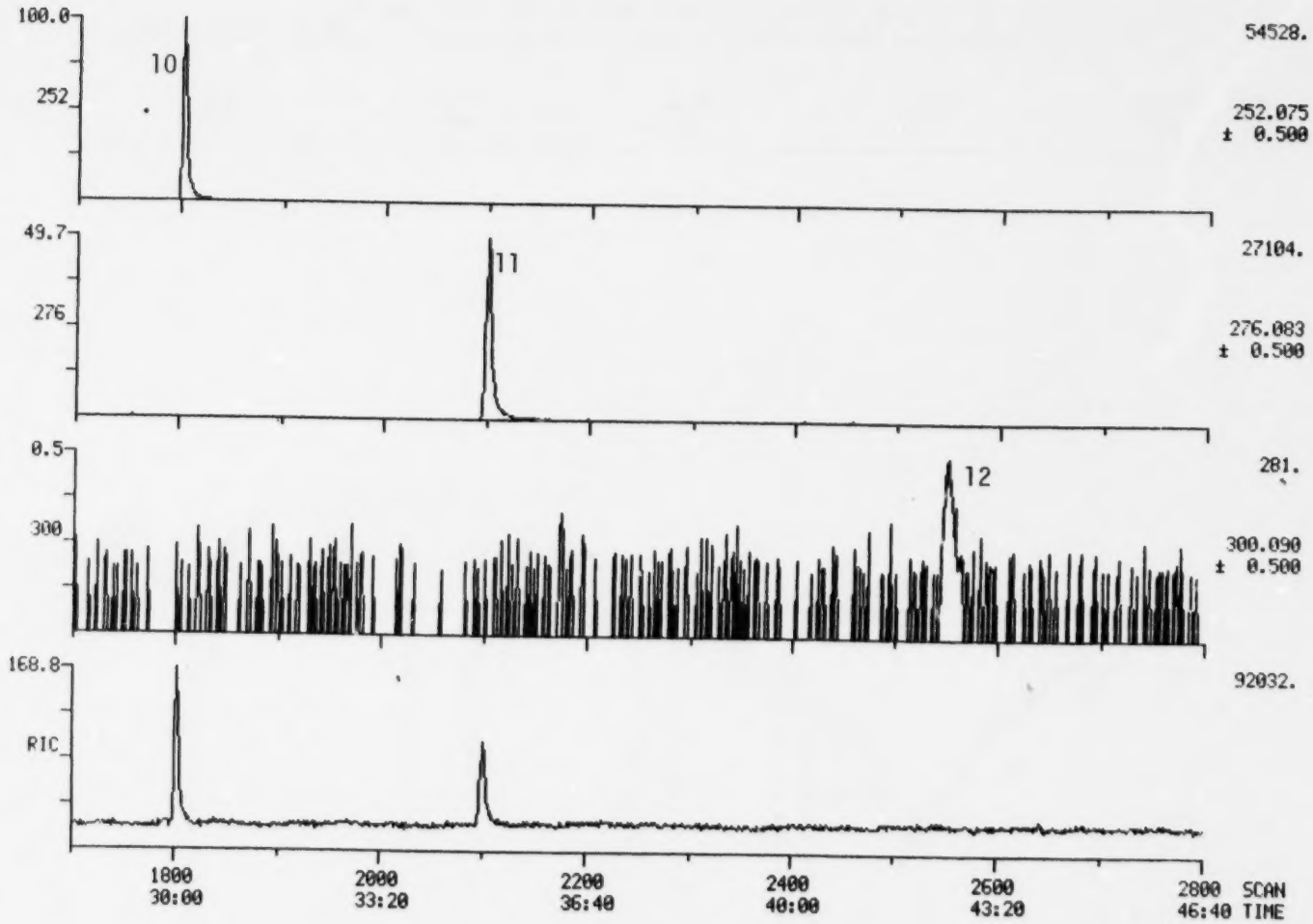

Figure A-3. (Continued)

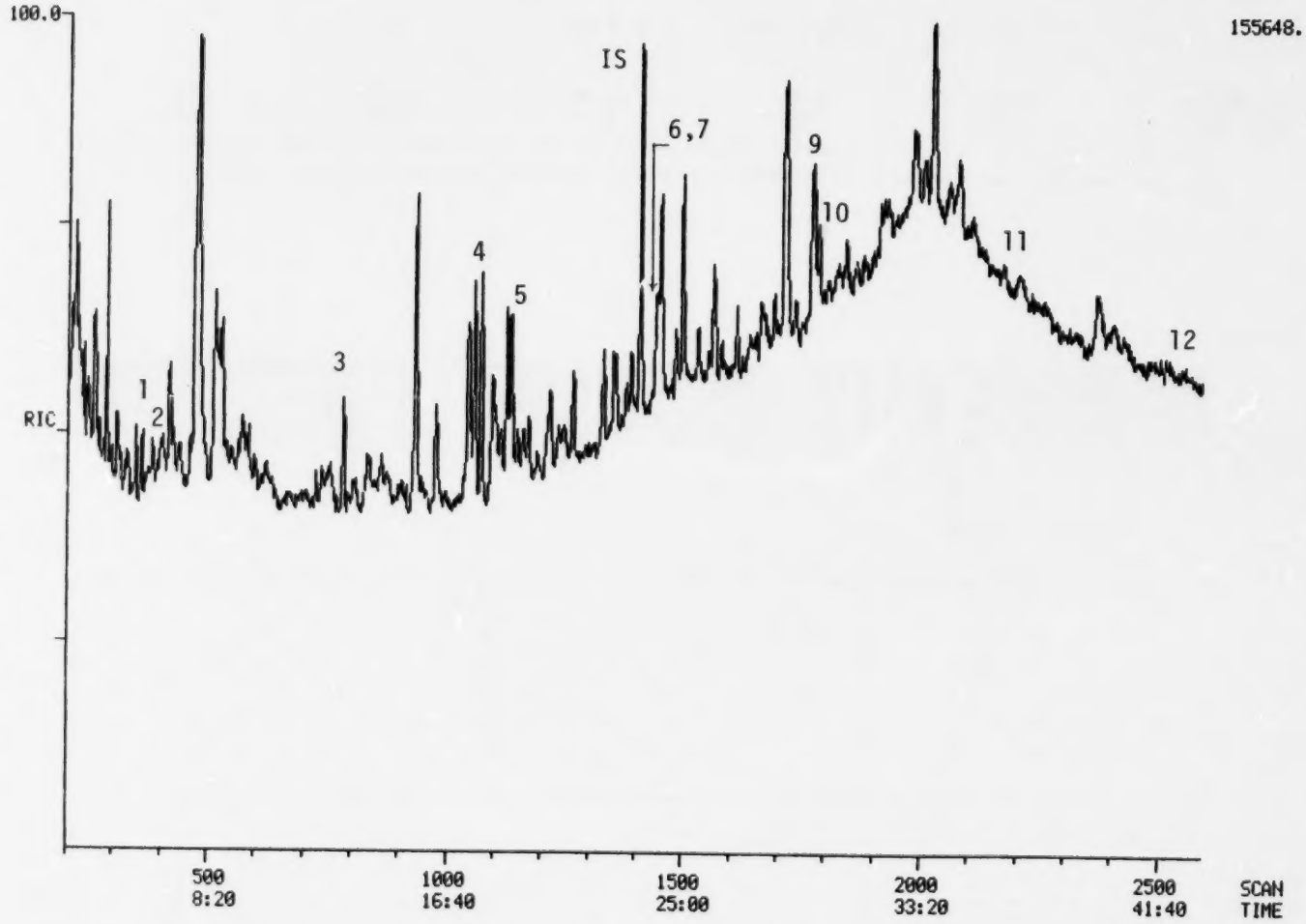

Figure A-4. Total ion current and selected ion current chromatograms from PCI GC/MS analysis of the nonfractionated air particulate extract.

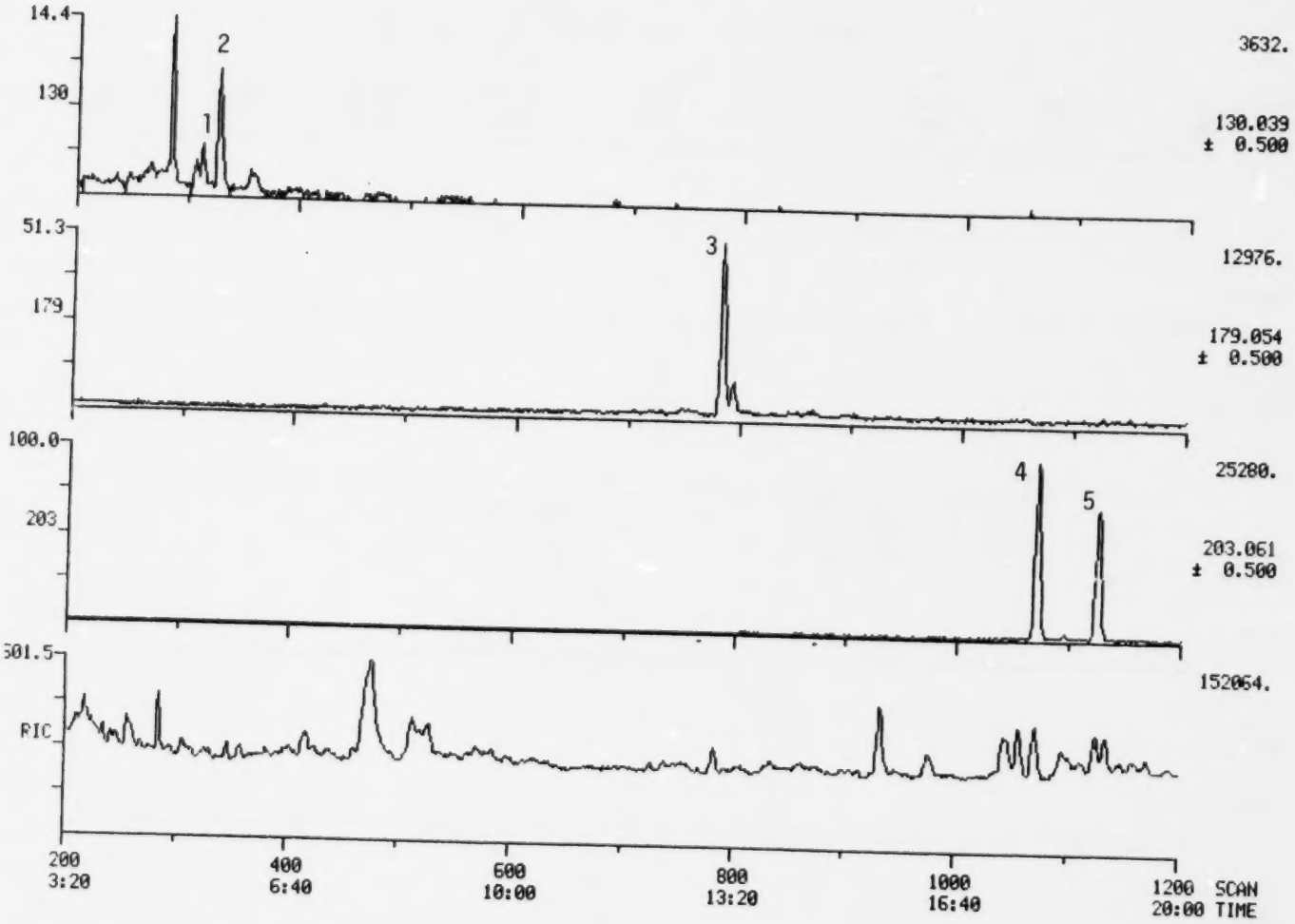

Figure A-4. (Continued)

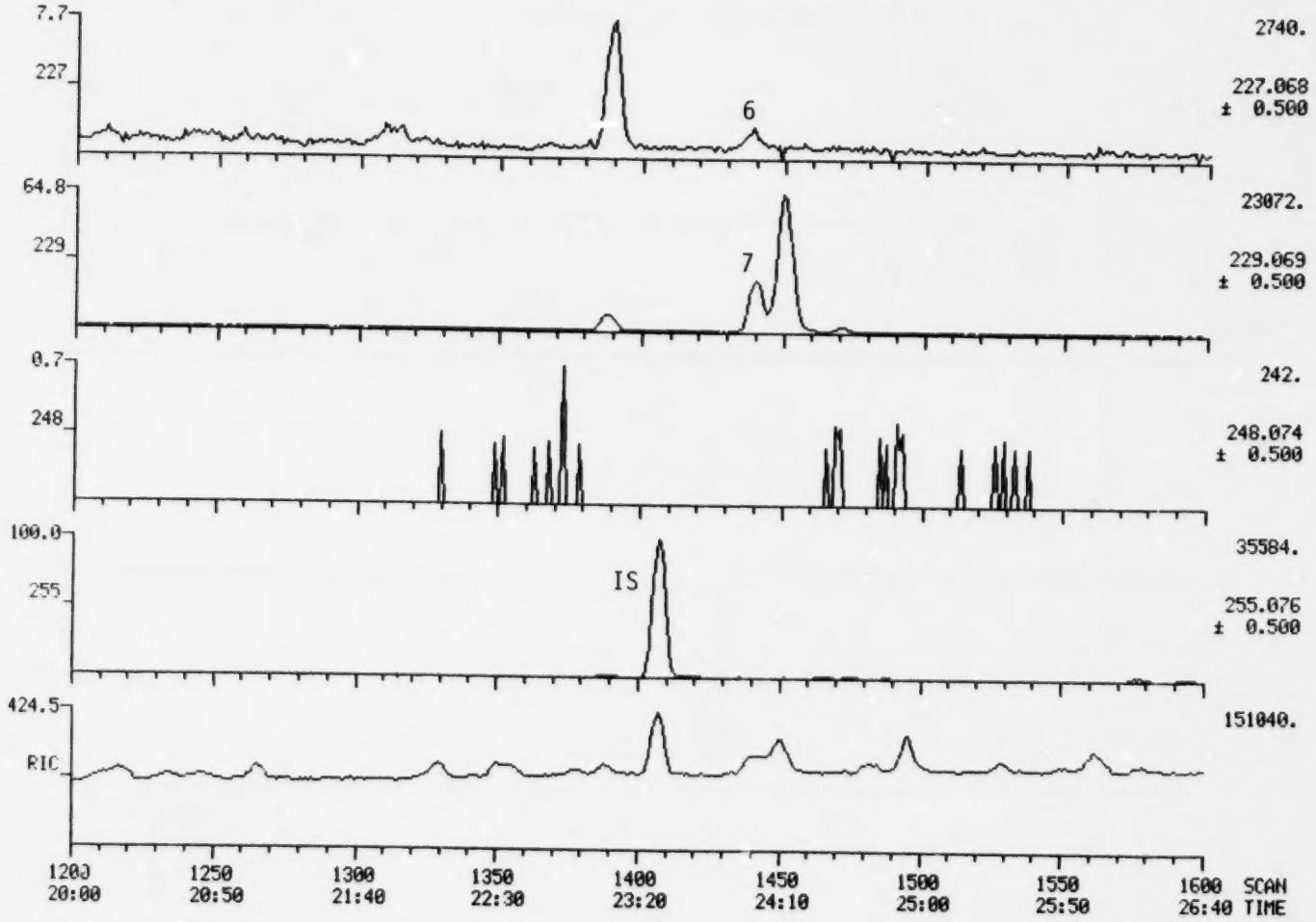

Figure A-4. (Continued)

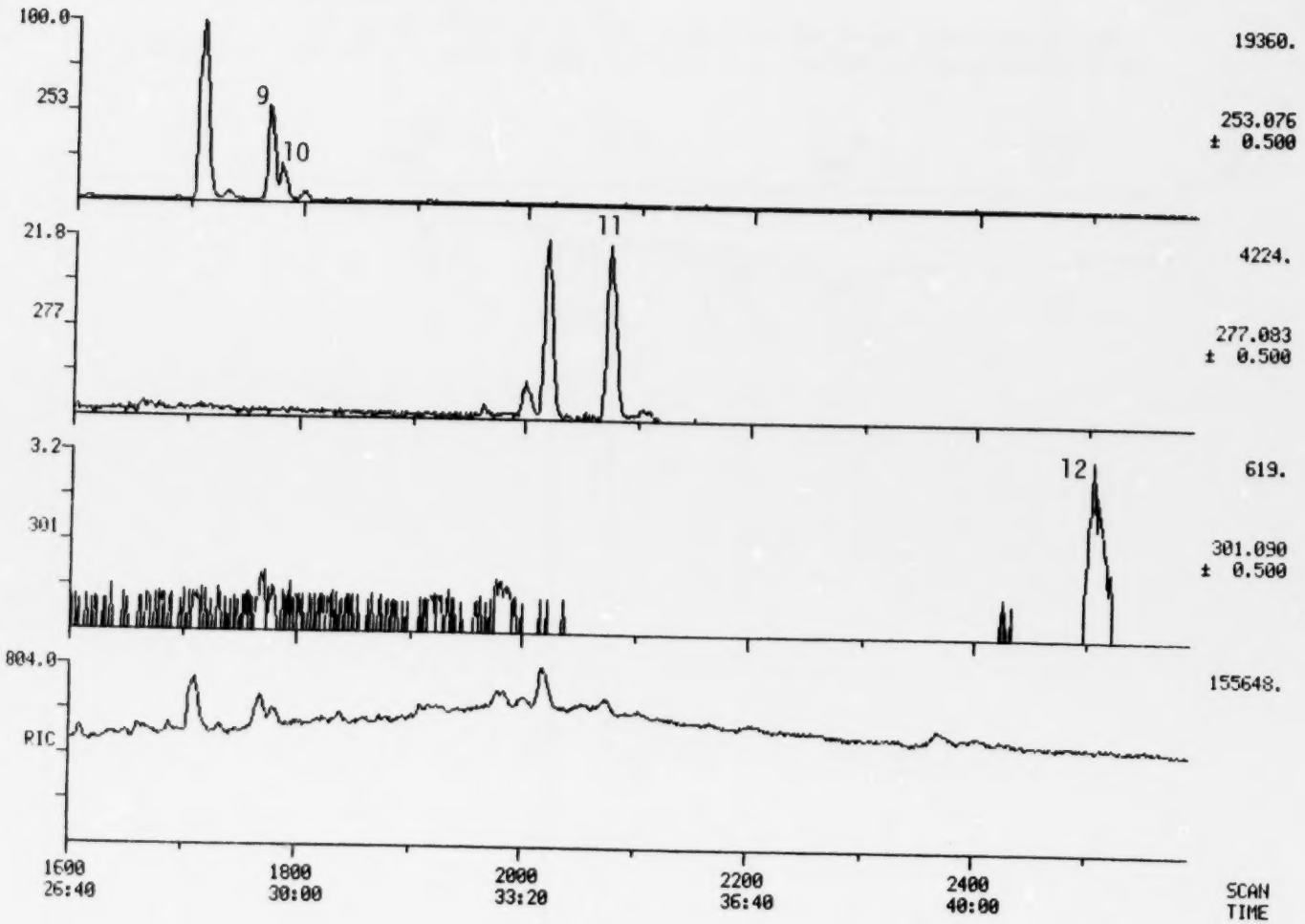

Figure A-4. (Continued)

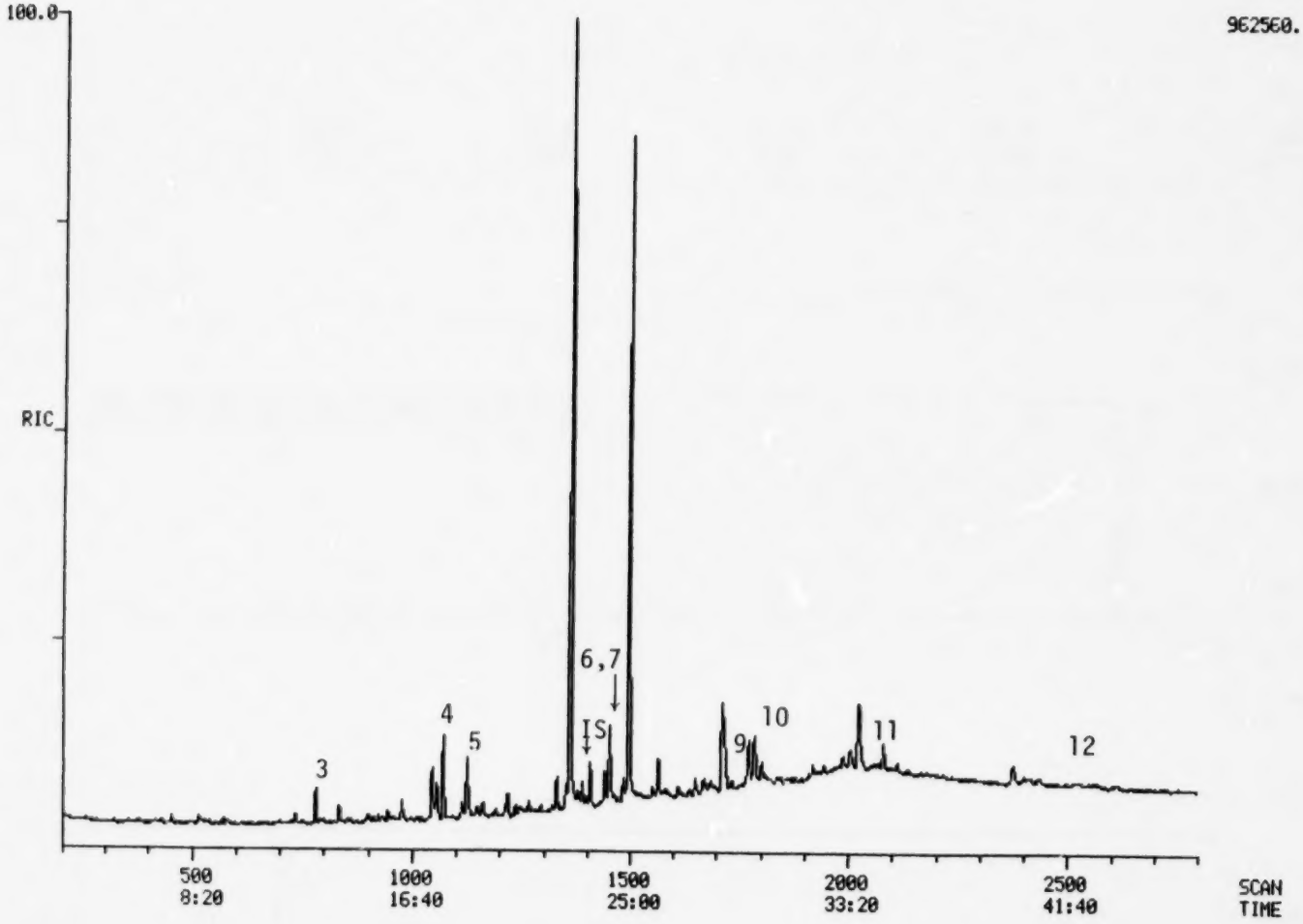

Figure A-5. Total ion current and selected ion current chromatograms from PCI GC/MS analysis of the methylene chloride fraction of the air particulate extract.

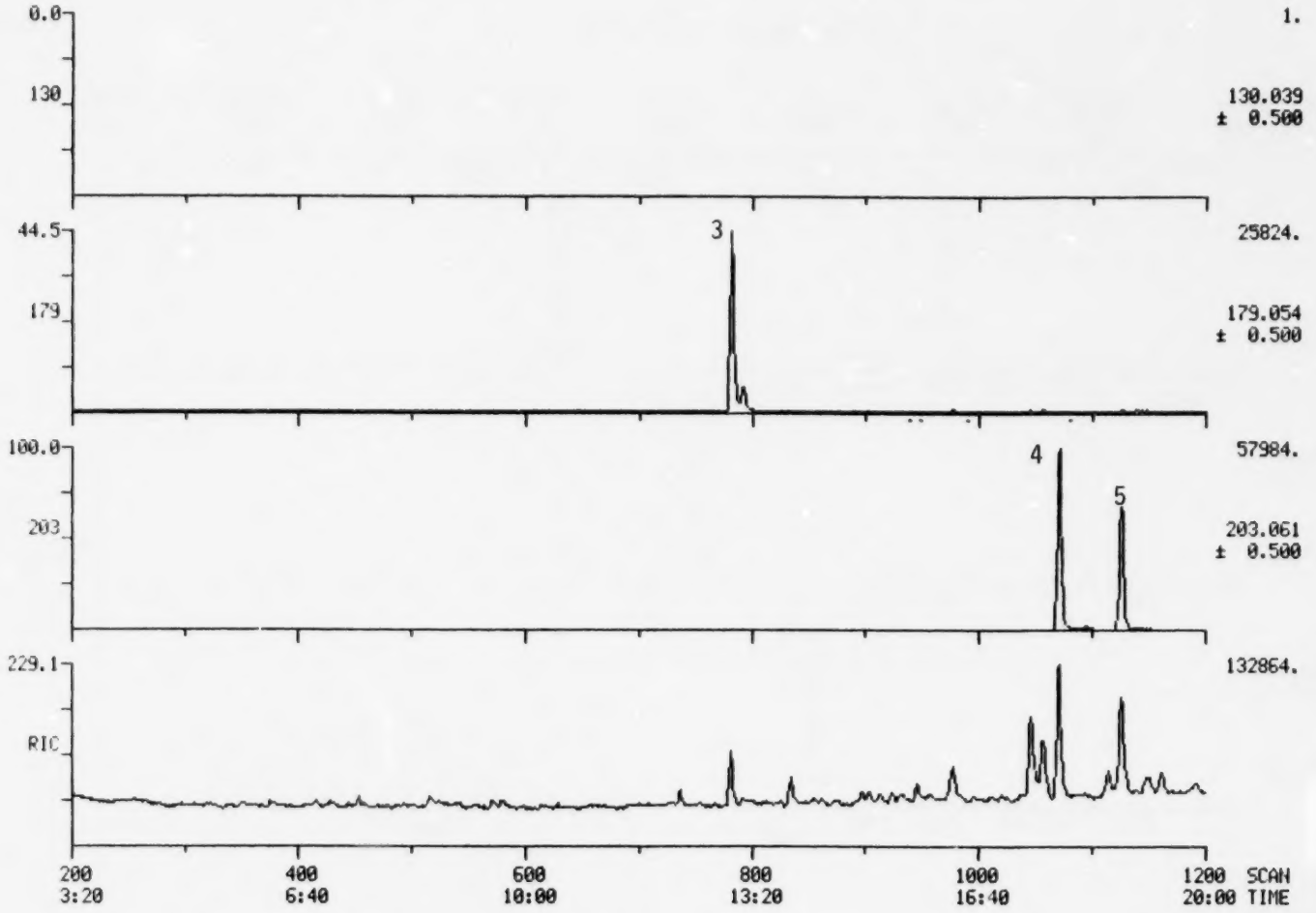

Figure A-5. (Continued)

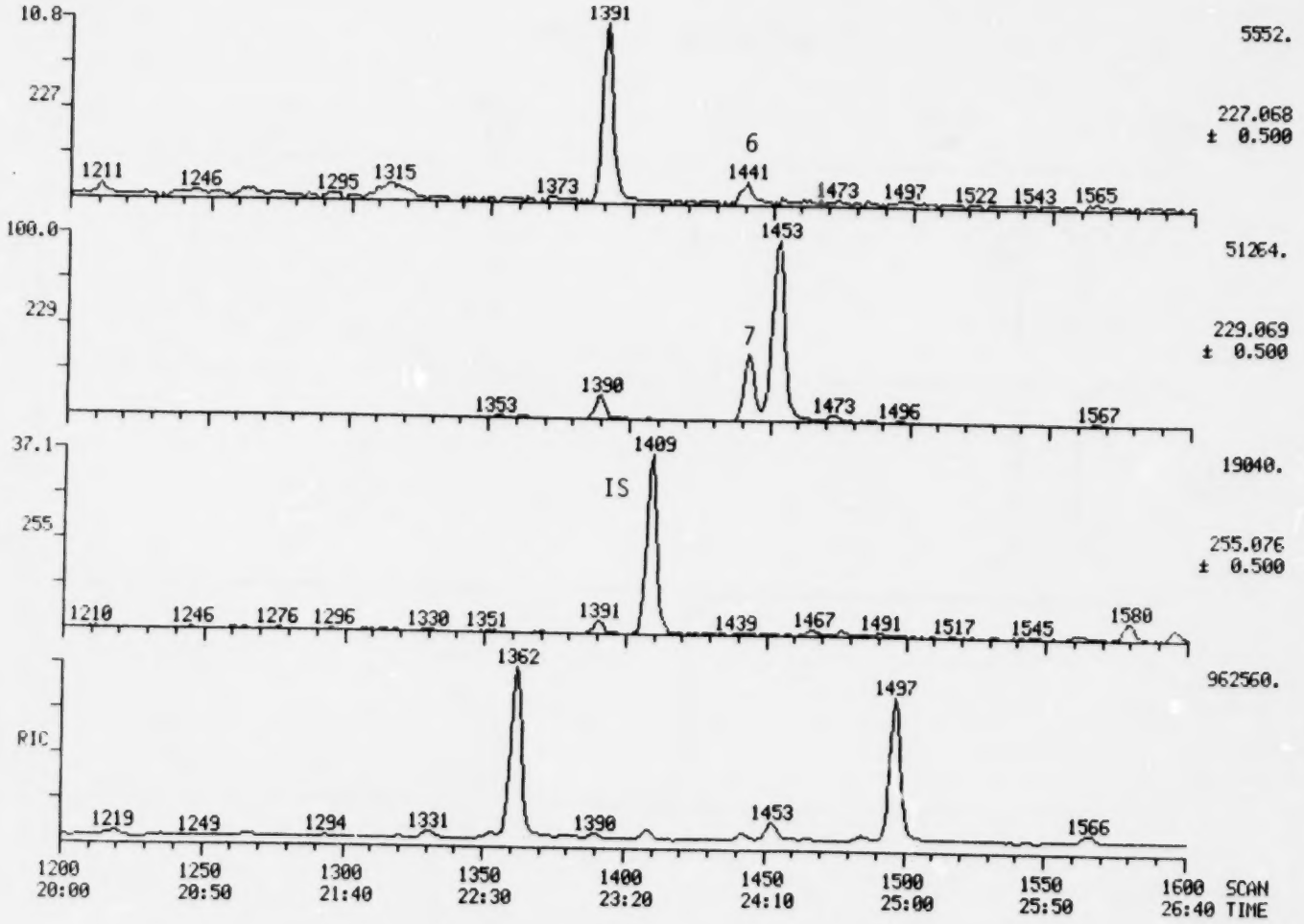

Figure A-5. (Continued)

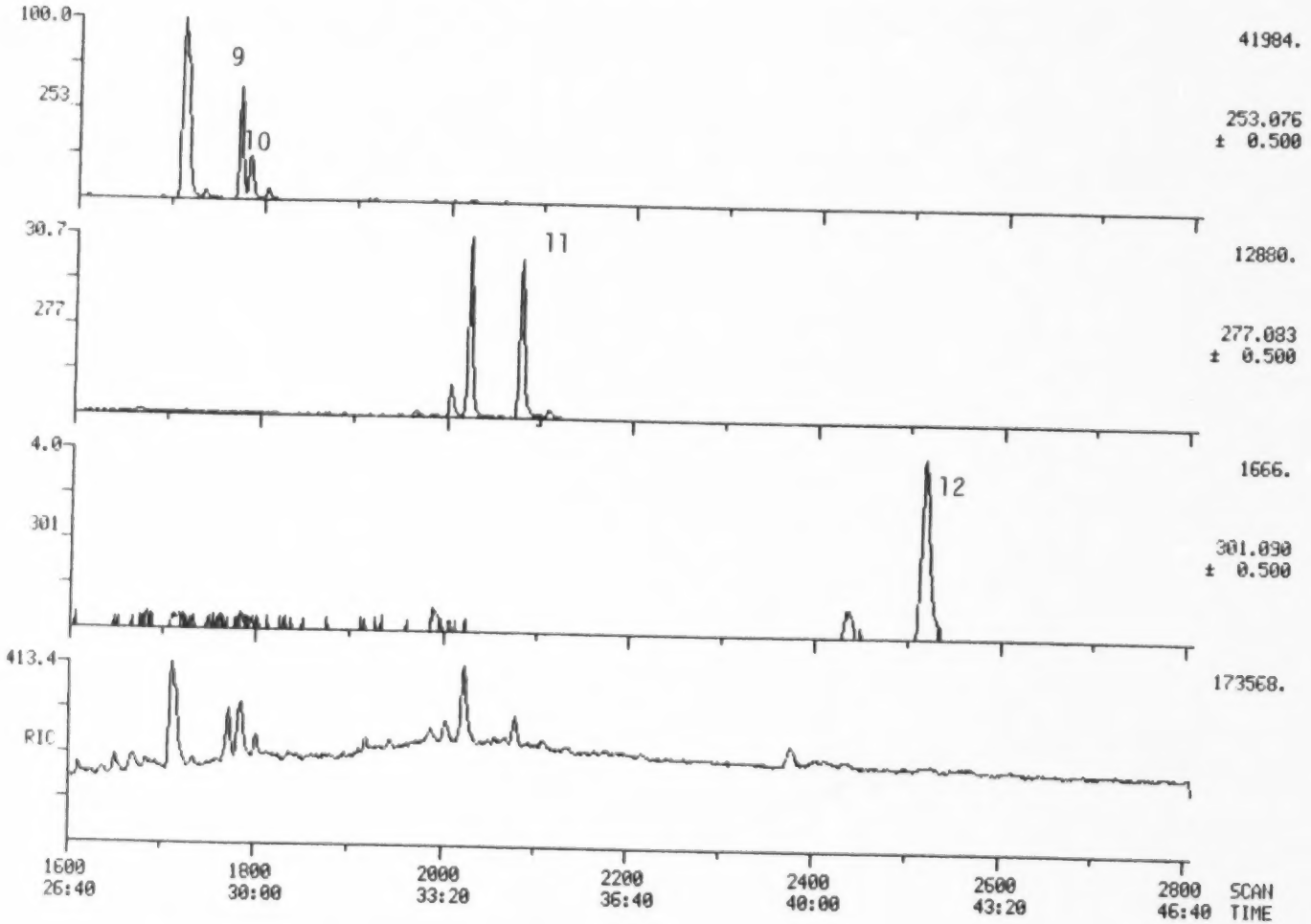

Figure A-5. (Continued)

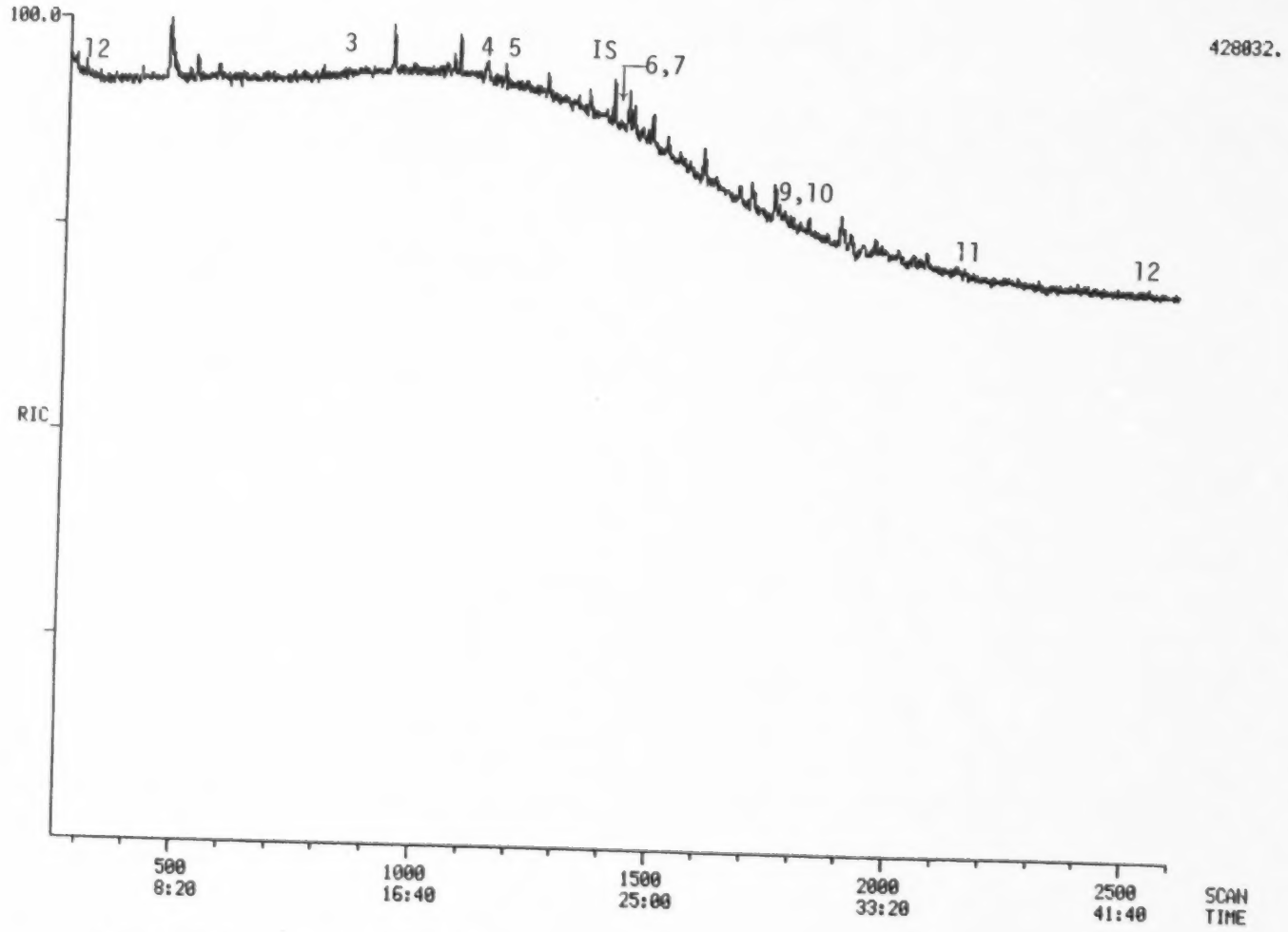

Figure A-6. Total ion current and selected ion current chromatograms from EI GC/MS analysis of the nonfractionated air particulate extract.

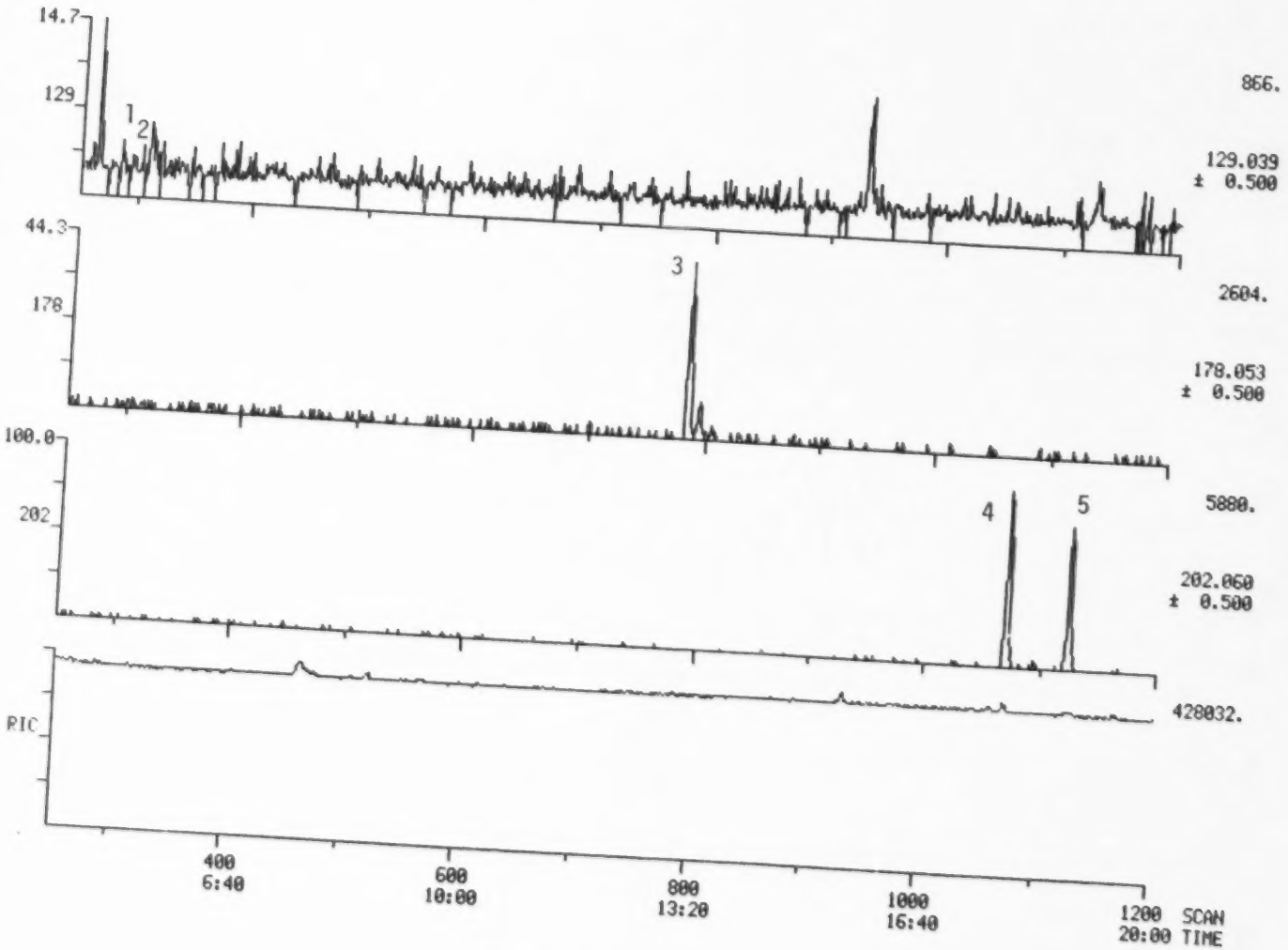

Figure A-6. (Continued)

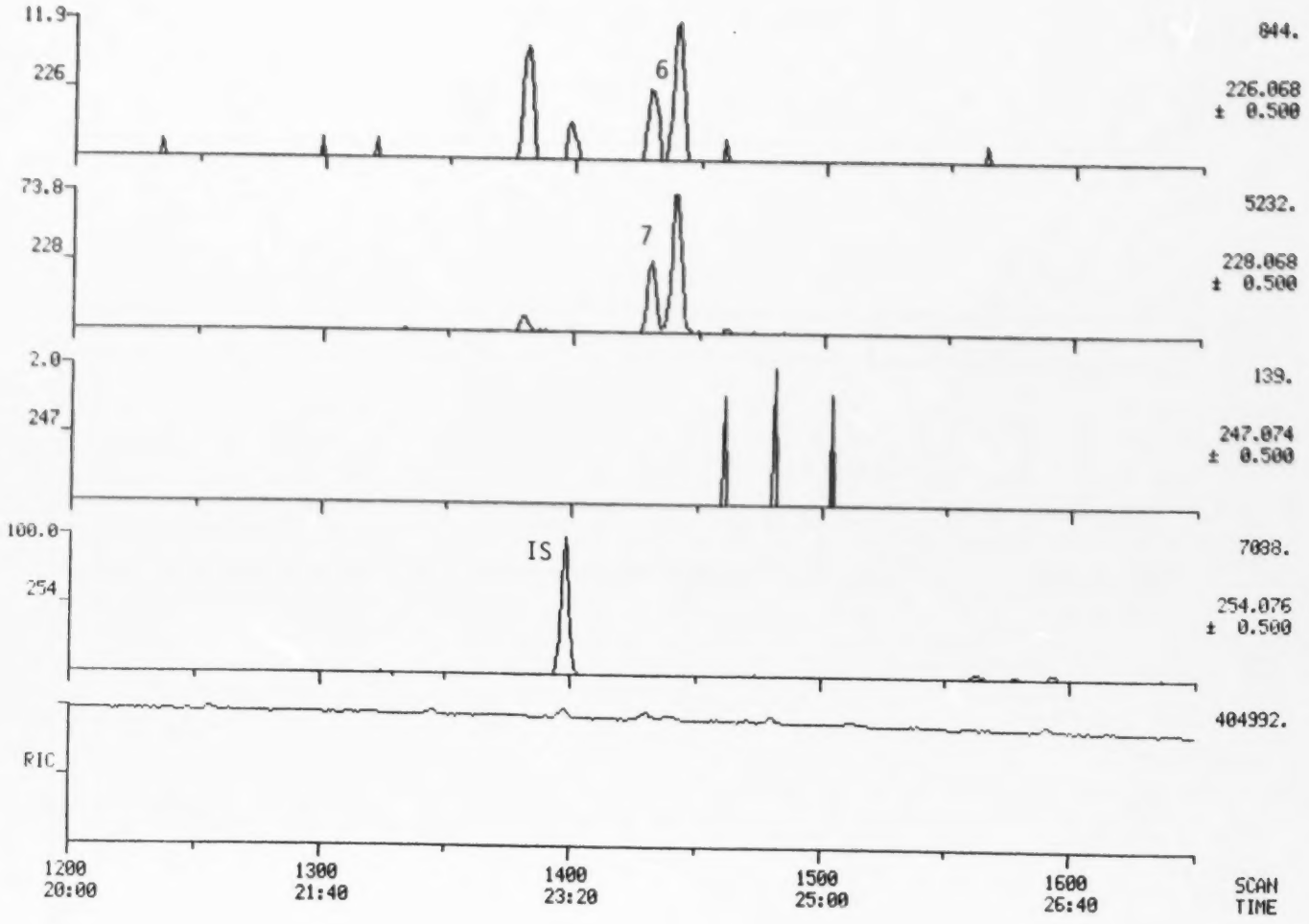

Figure A-6. (Continued)

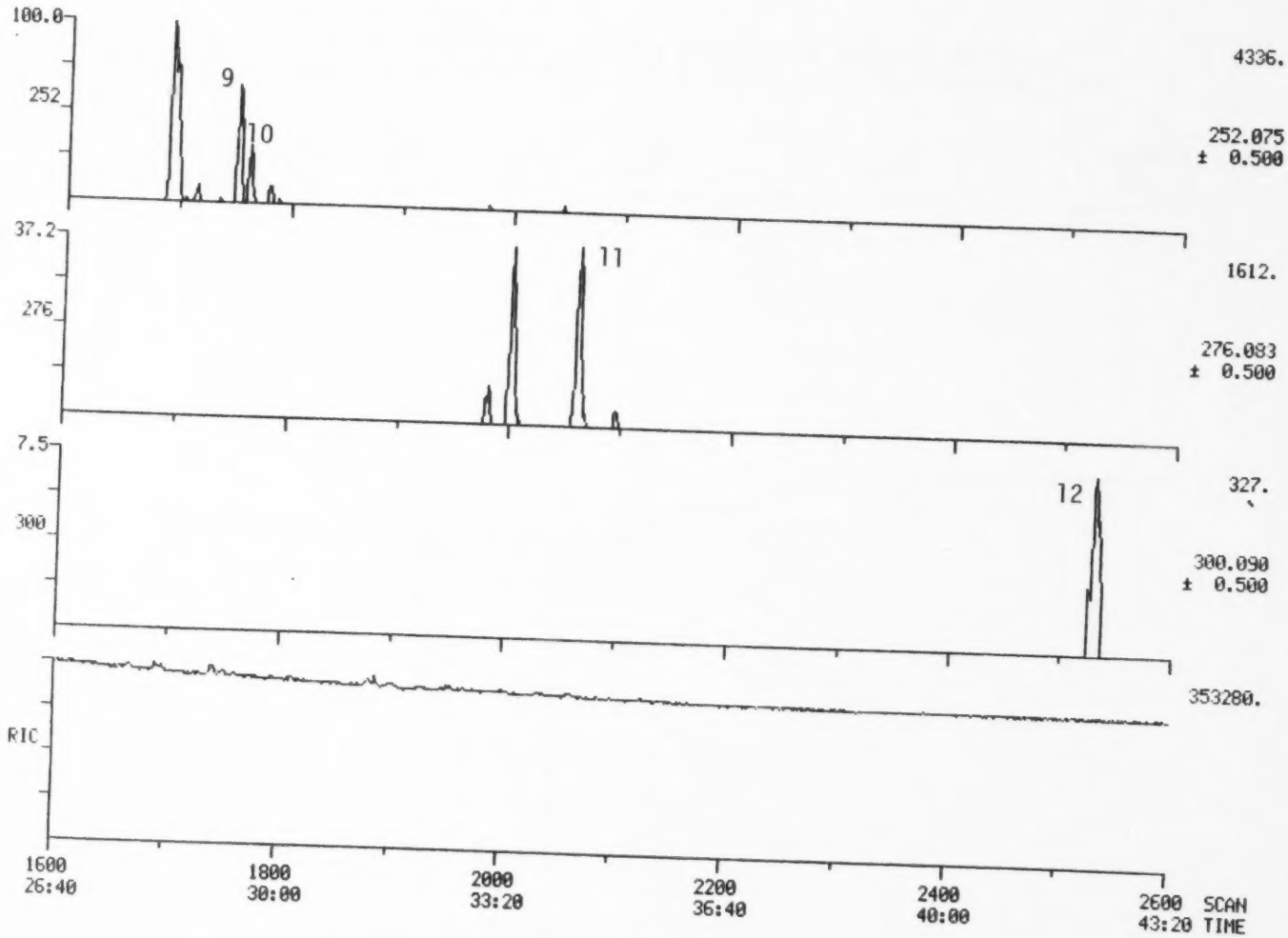

Figure A-6. (Continued)

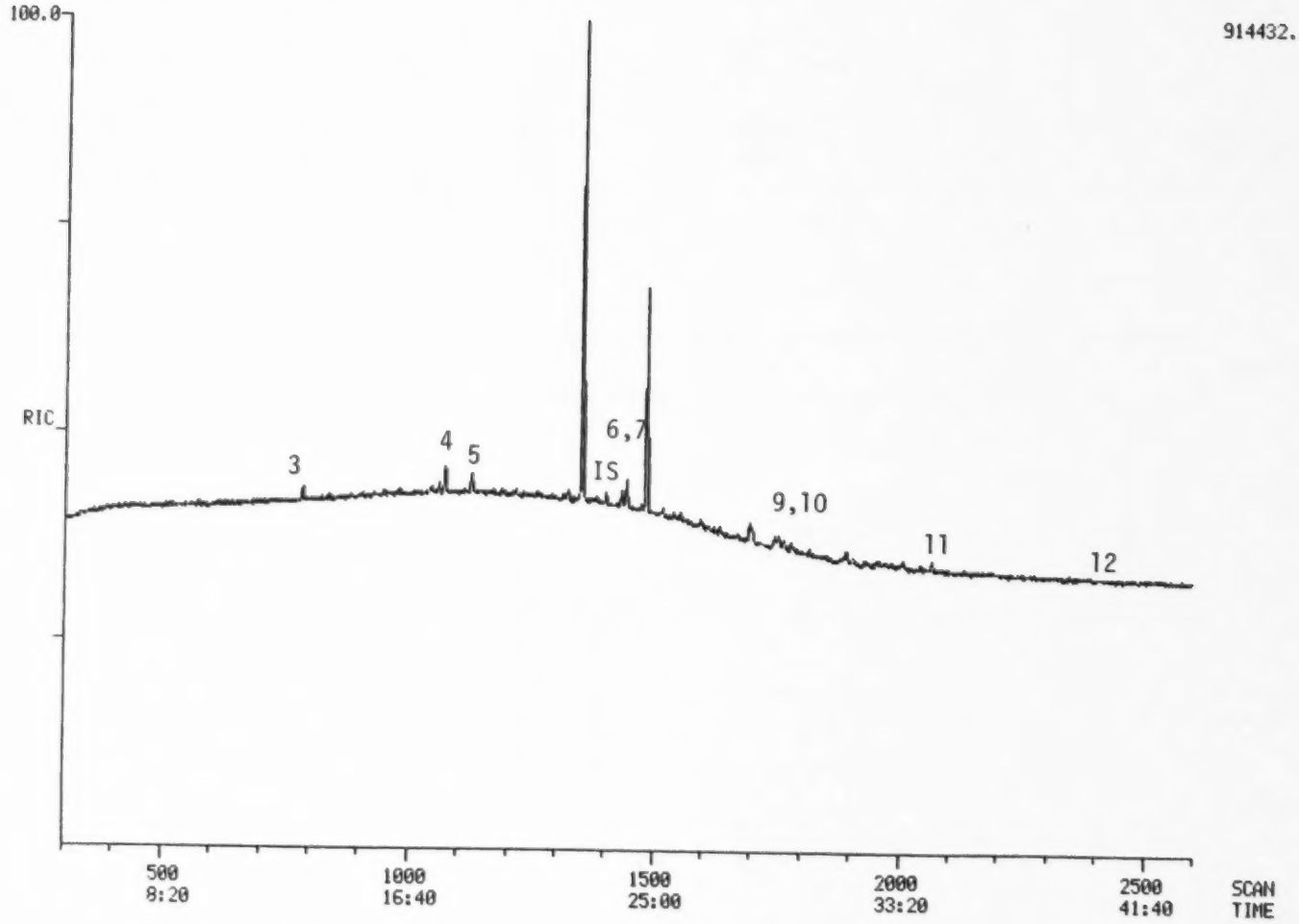

Figure A-7. Total ion current and selected ion current chromatograms from EI GC/MS analysis of the air particulate extract methylene chloride fraction.

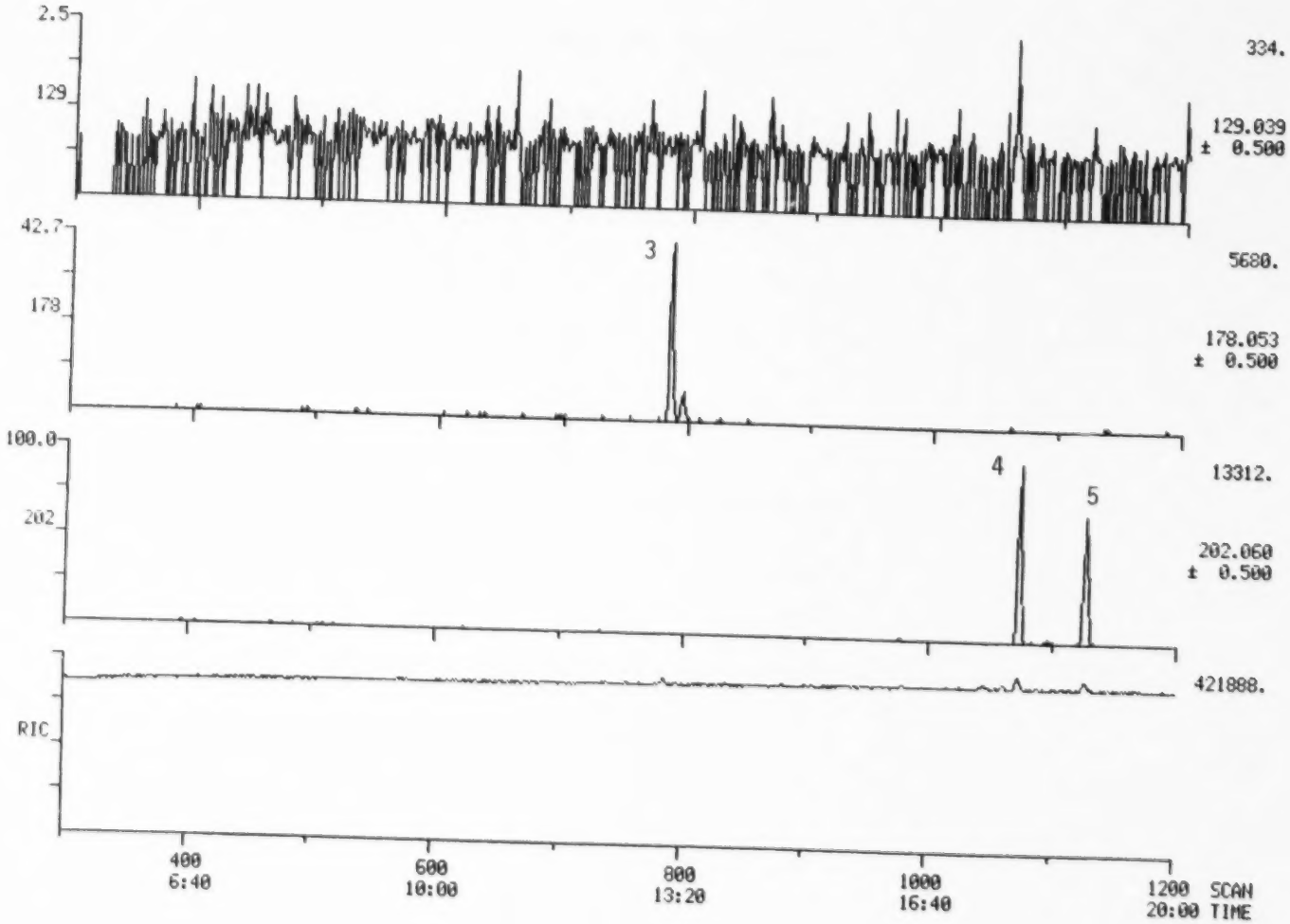

Figure A-7. (Continued)

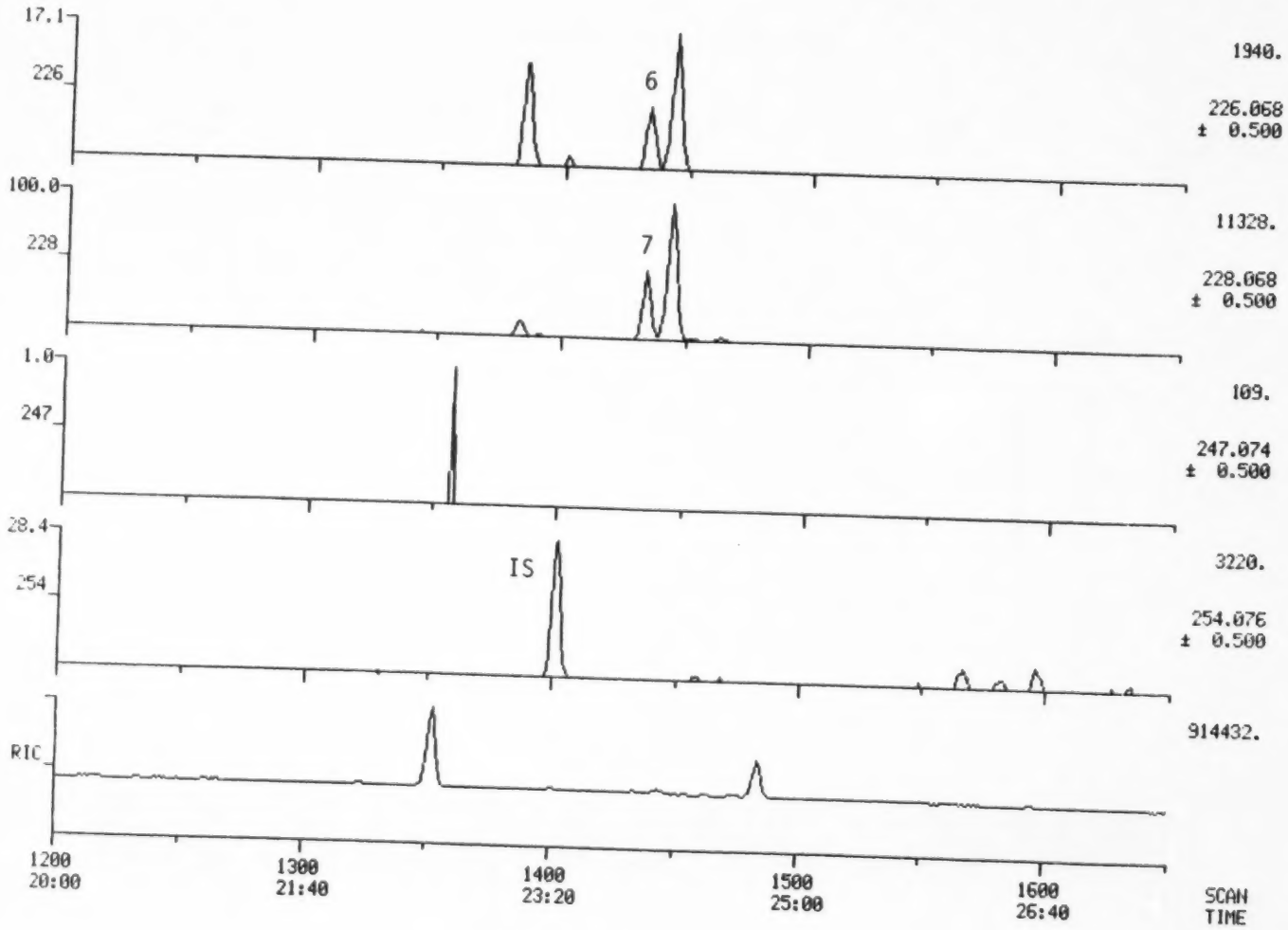

Figure A-7. (Continued)

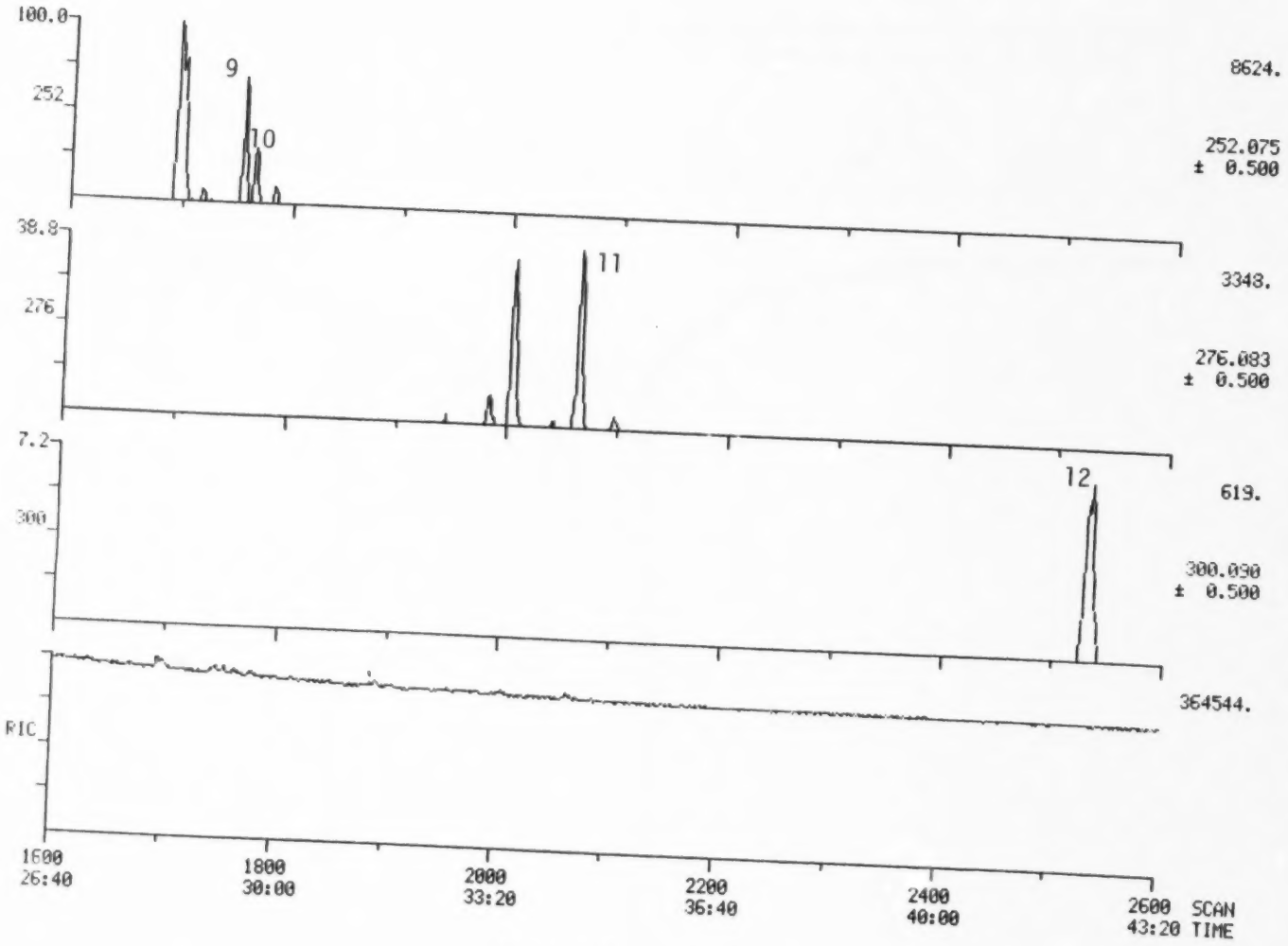

Figure A-7. (Continued)

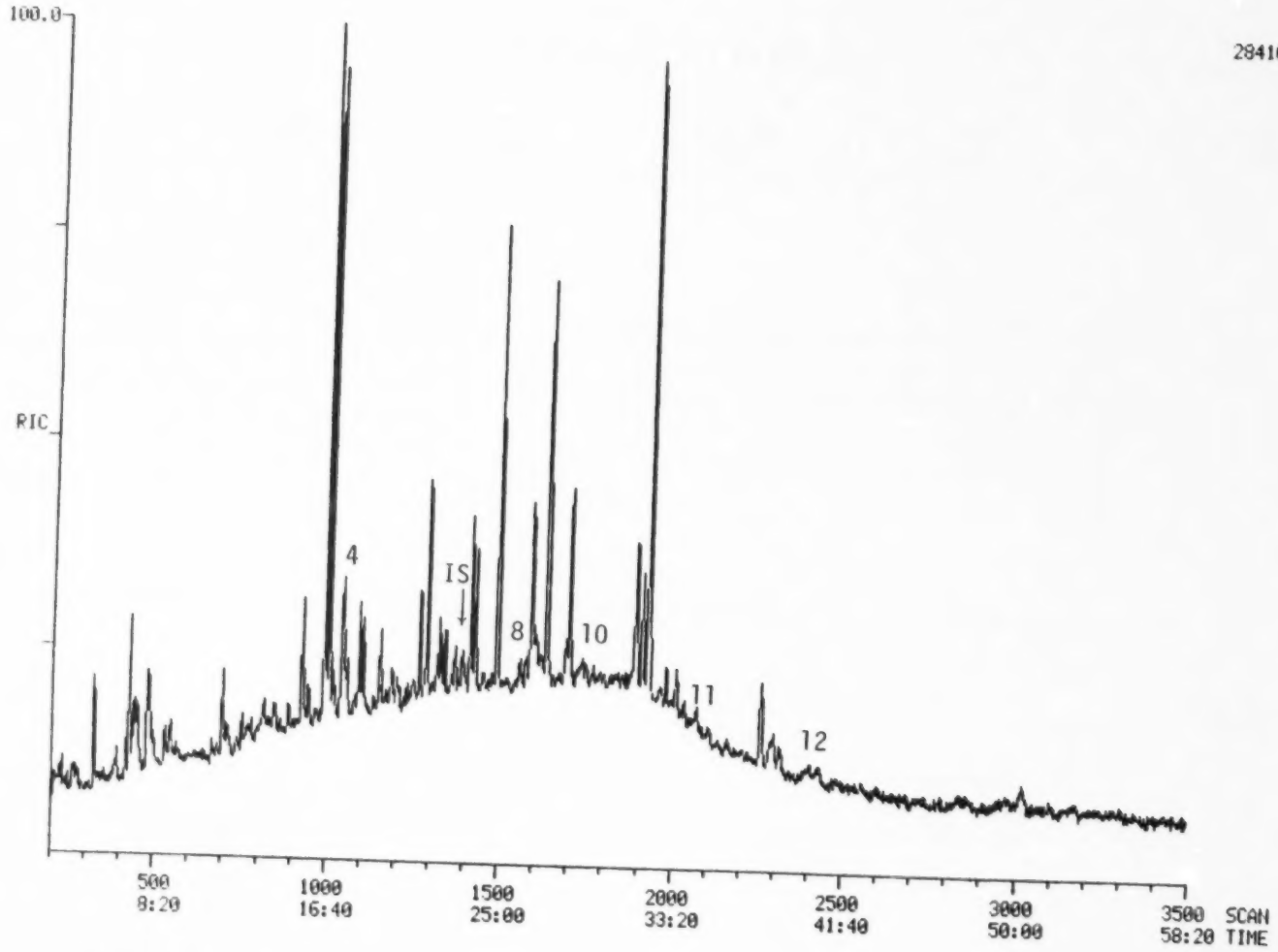

Figure A-8. Total ion current and selected ion current chromatograms from NCI GC/MS analysis of the nonfractionated air particulate extract

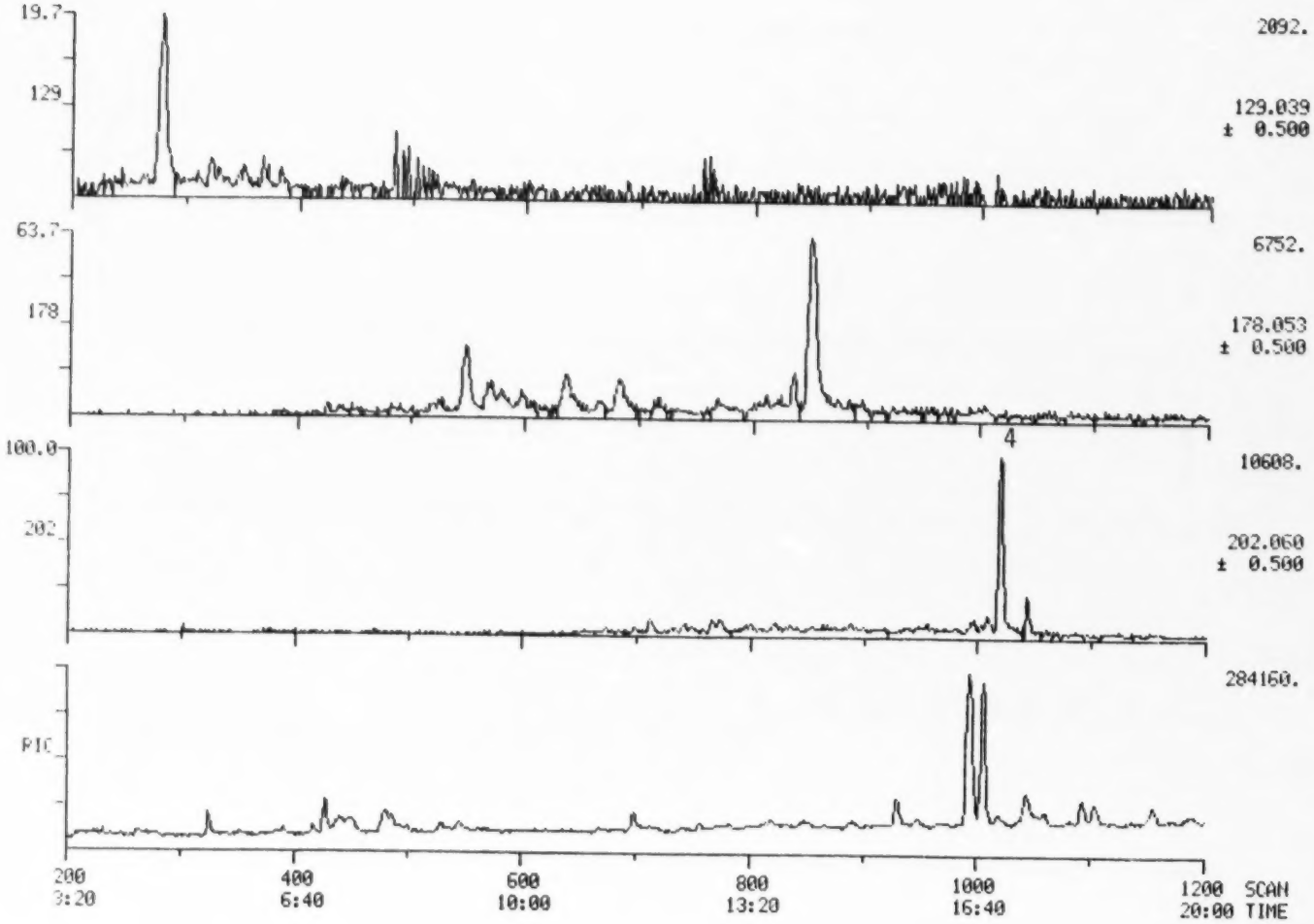

Figure A-8. (Continued)

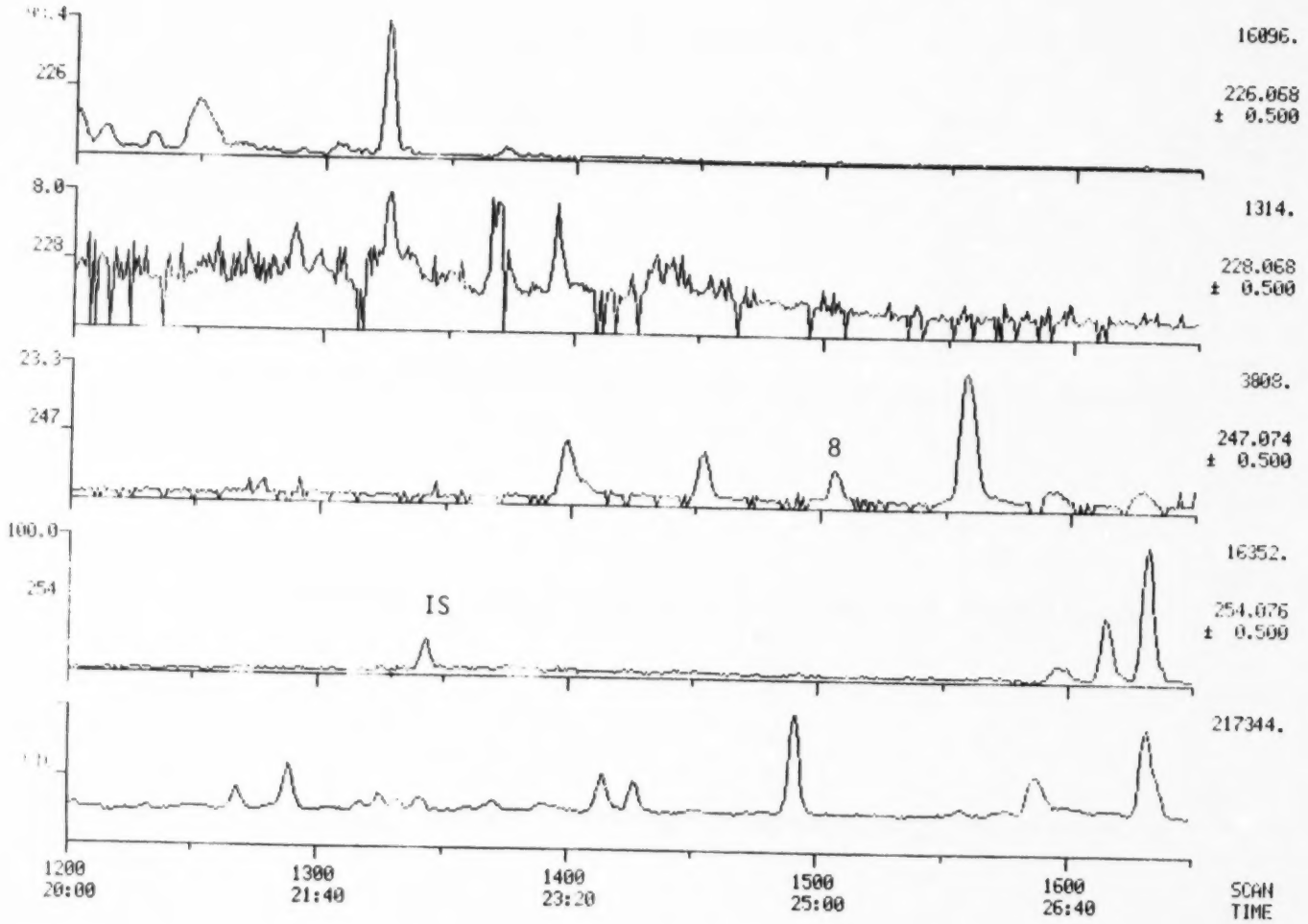

Figure A-8. (Continued)

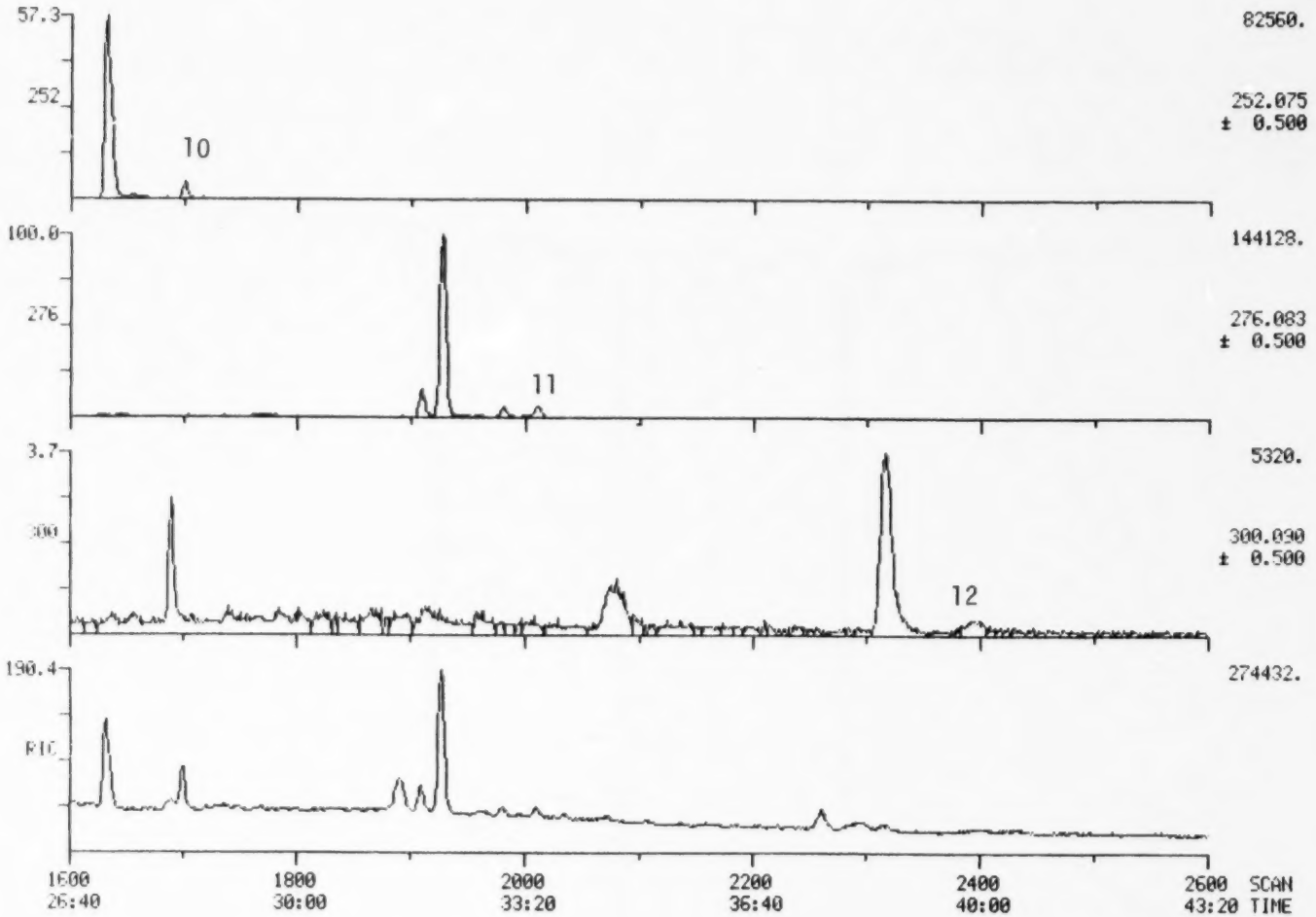

Figure A-8. (Continued)

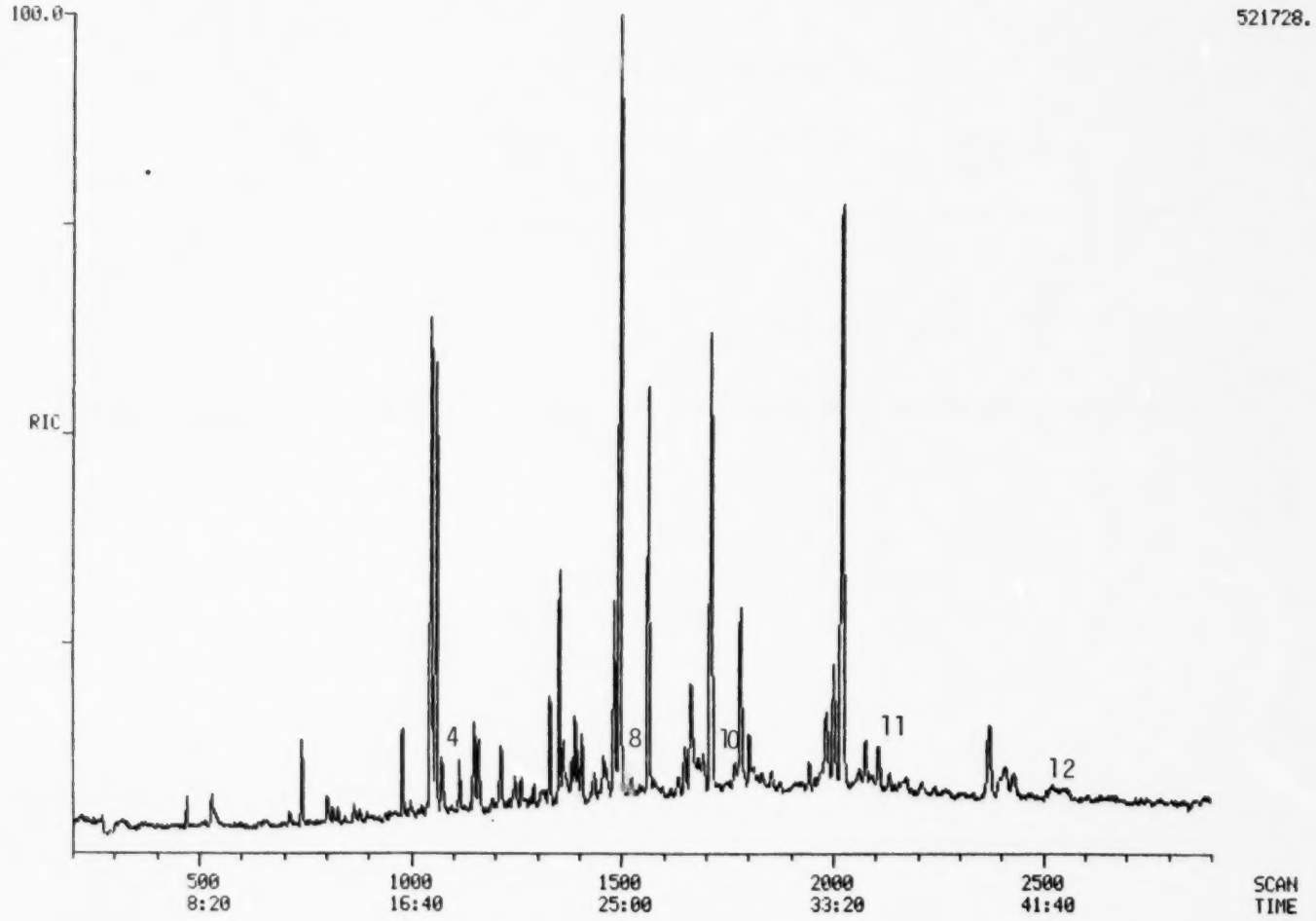

Figure A-9. Total ion current and selected ion current chromatograms from NCI GC/MS analysis of the methylene chloride fraction of the air particulate extract.

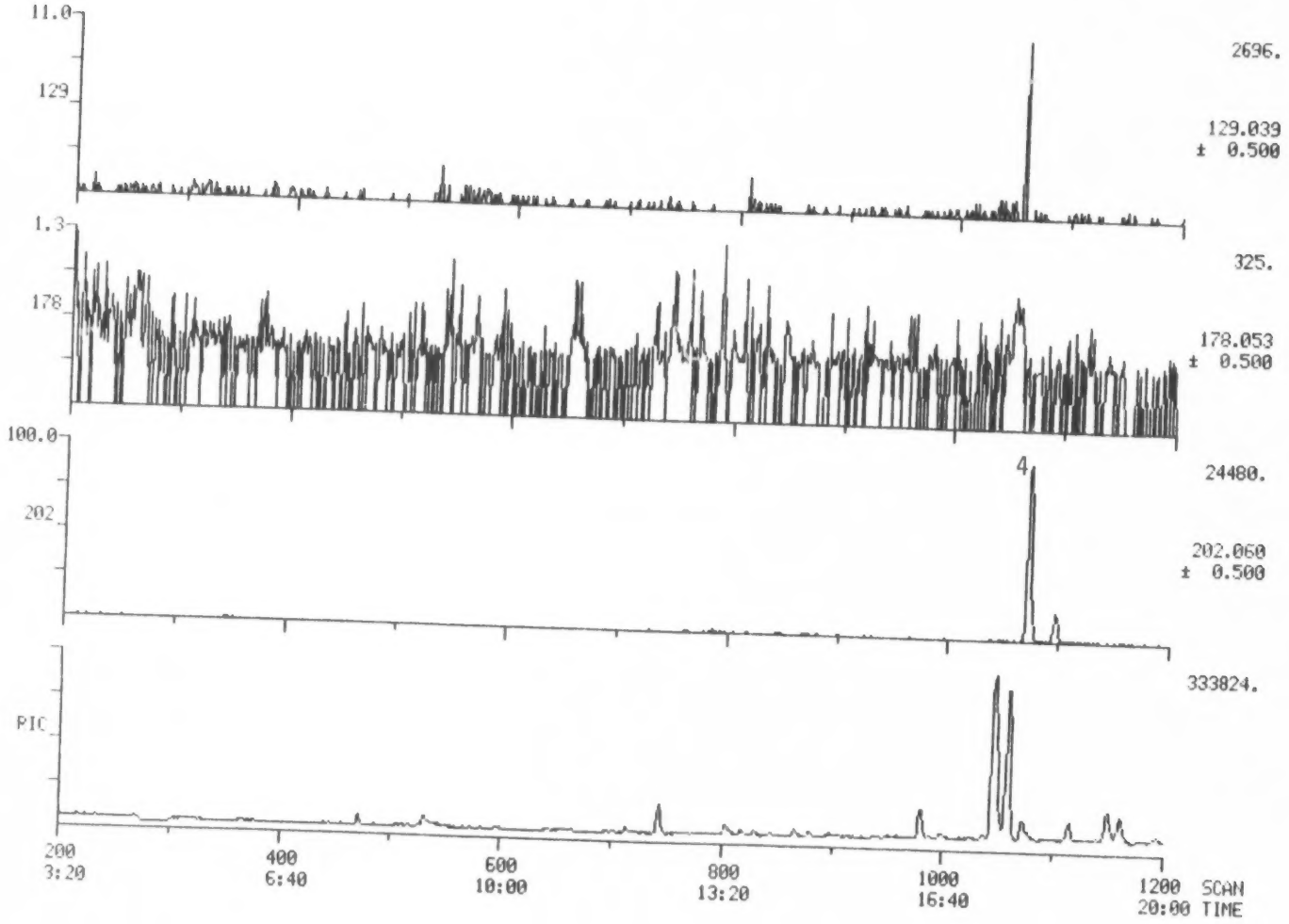

Figure A-9. (Continued)

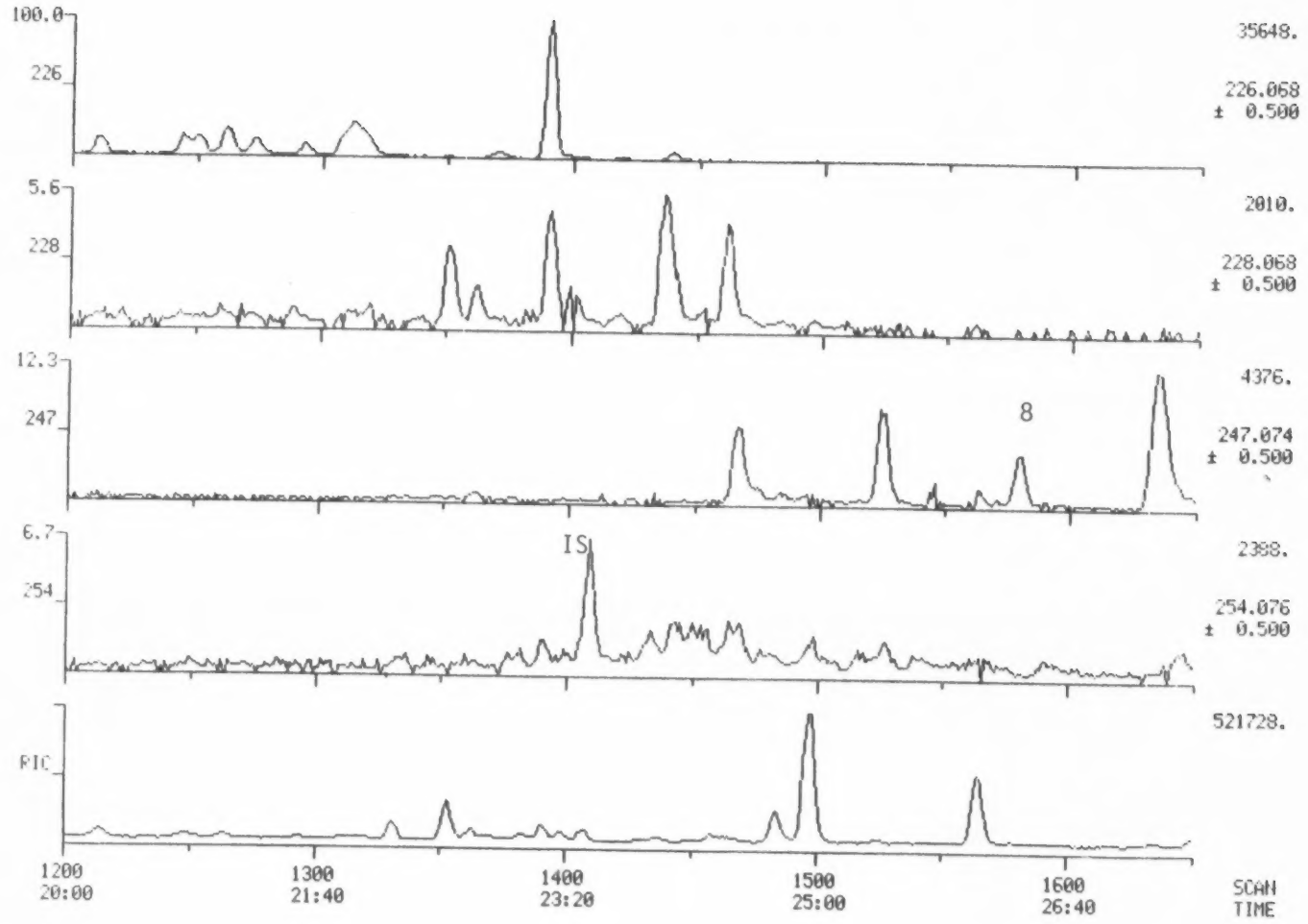

Figure A-9. (Continued)

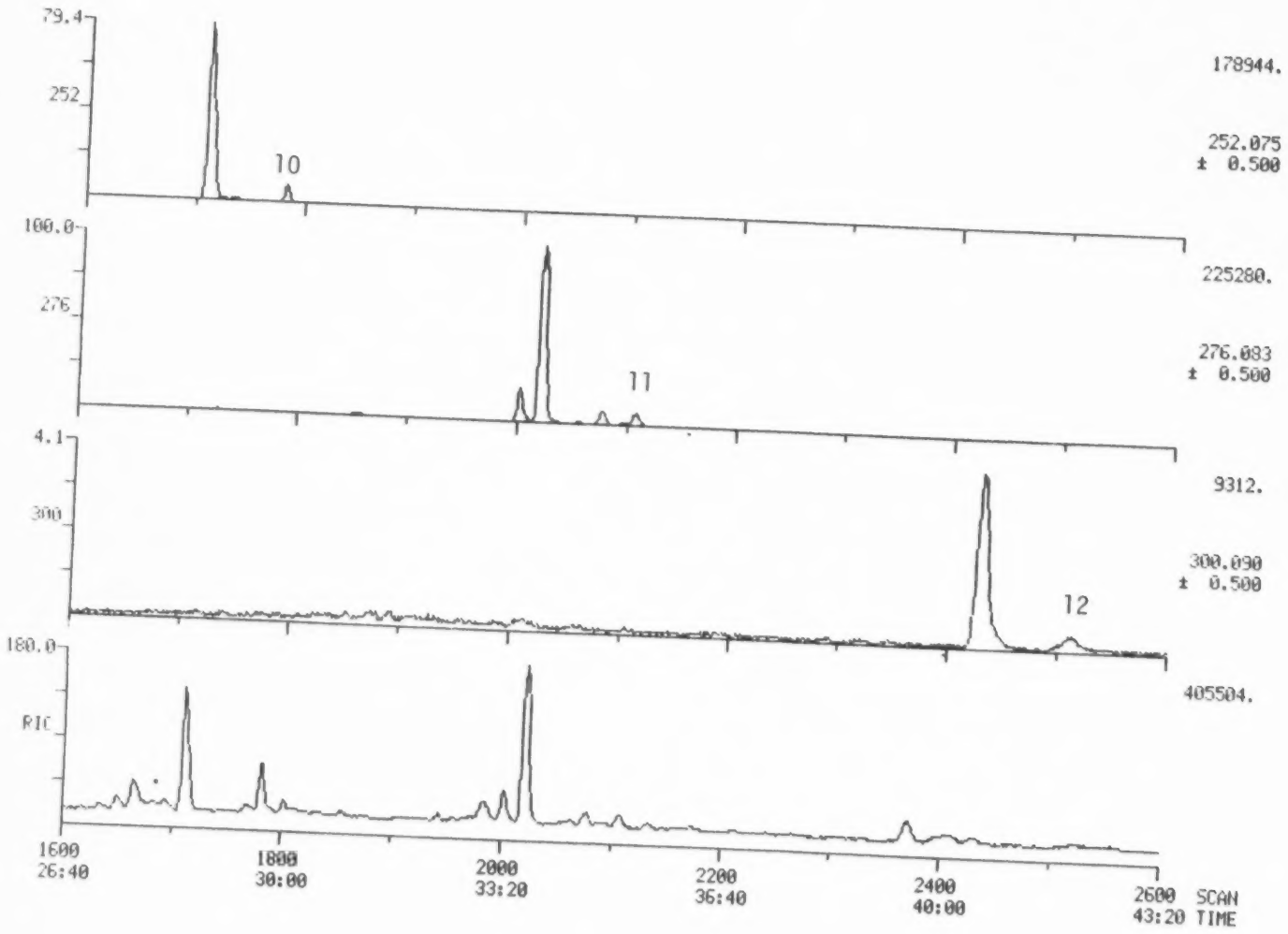

Figure A-9. (Continued)

APPENDIX B

CHROMATOGRAMS FROM HPLC ANALYSIS OF THE AIR PARTICULATE EXTRACT SAMPLES

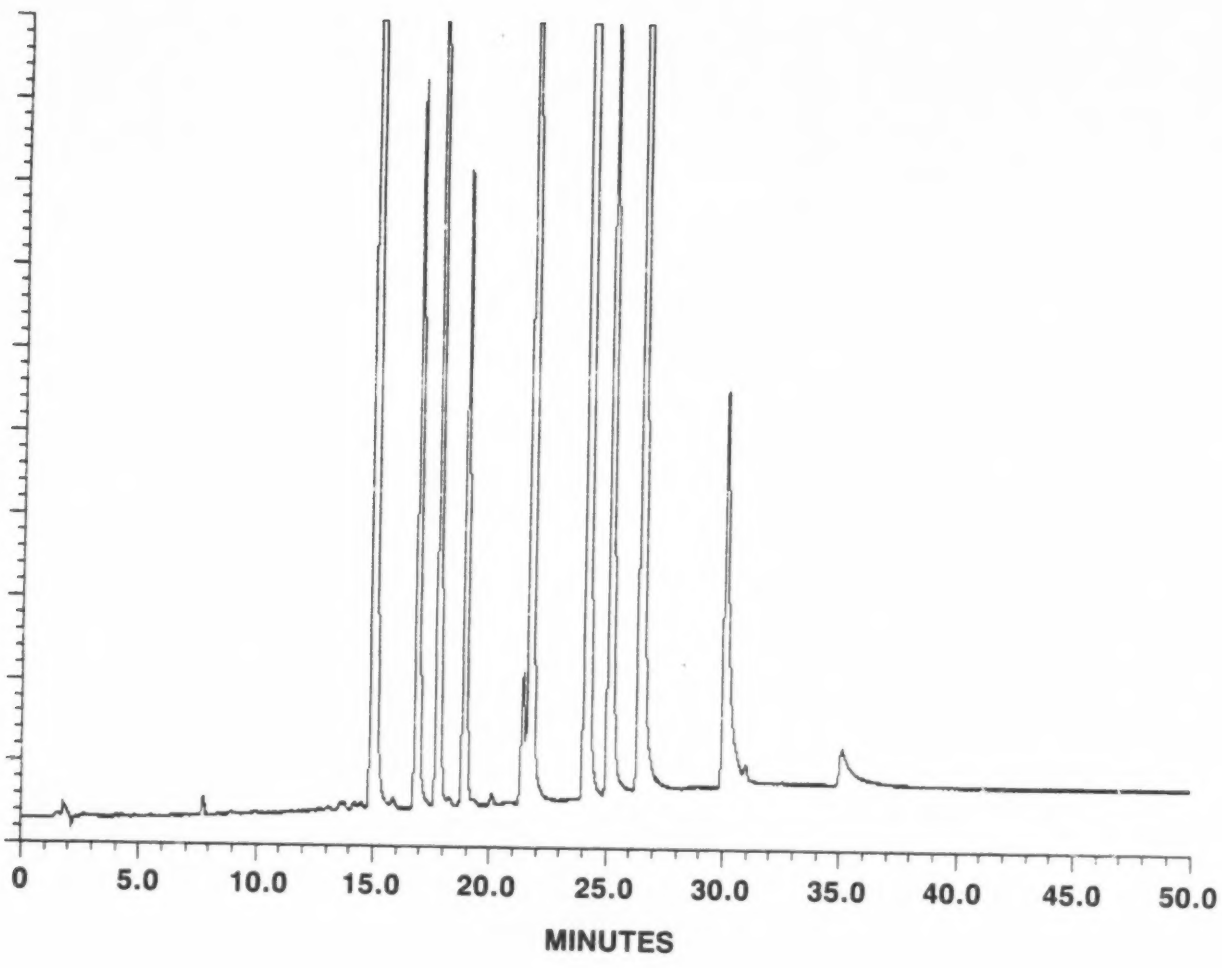

Figure B-1. The chromatogram from HPLC analysis with UV detection of the target compound standard solution.

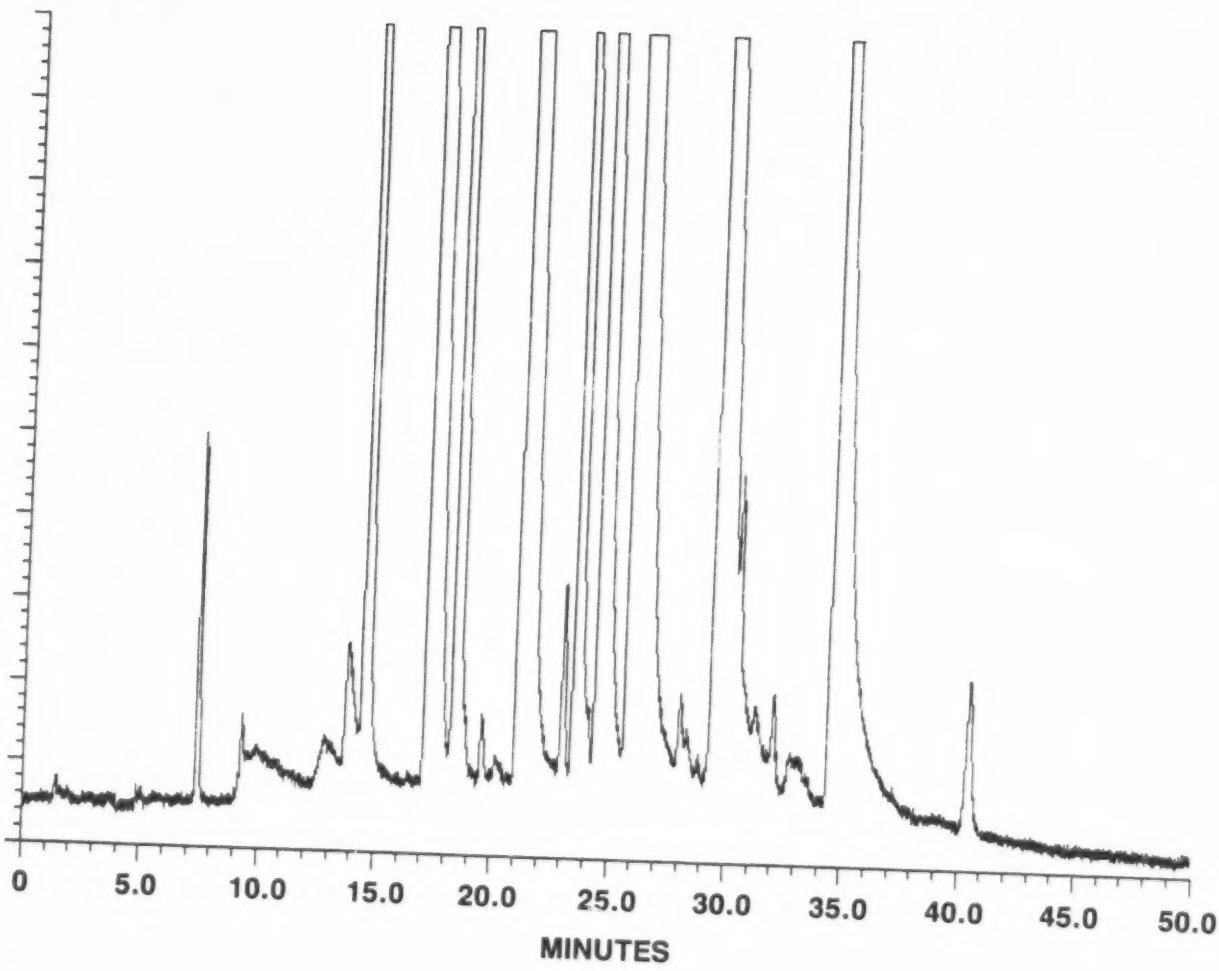

Figure B-2. The chromatogram from HPLC analysis with fluorescence detection of the target compound standard solution.

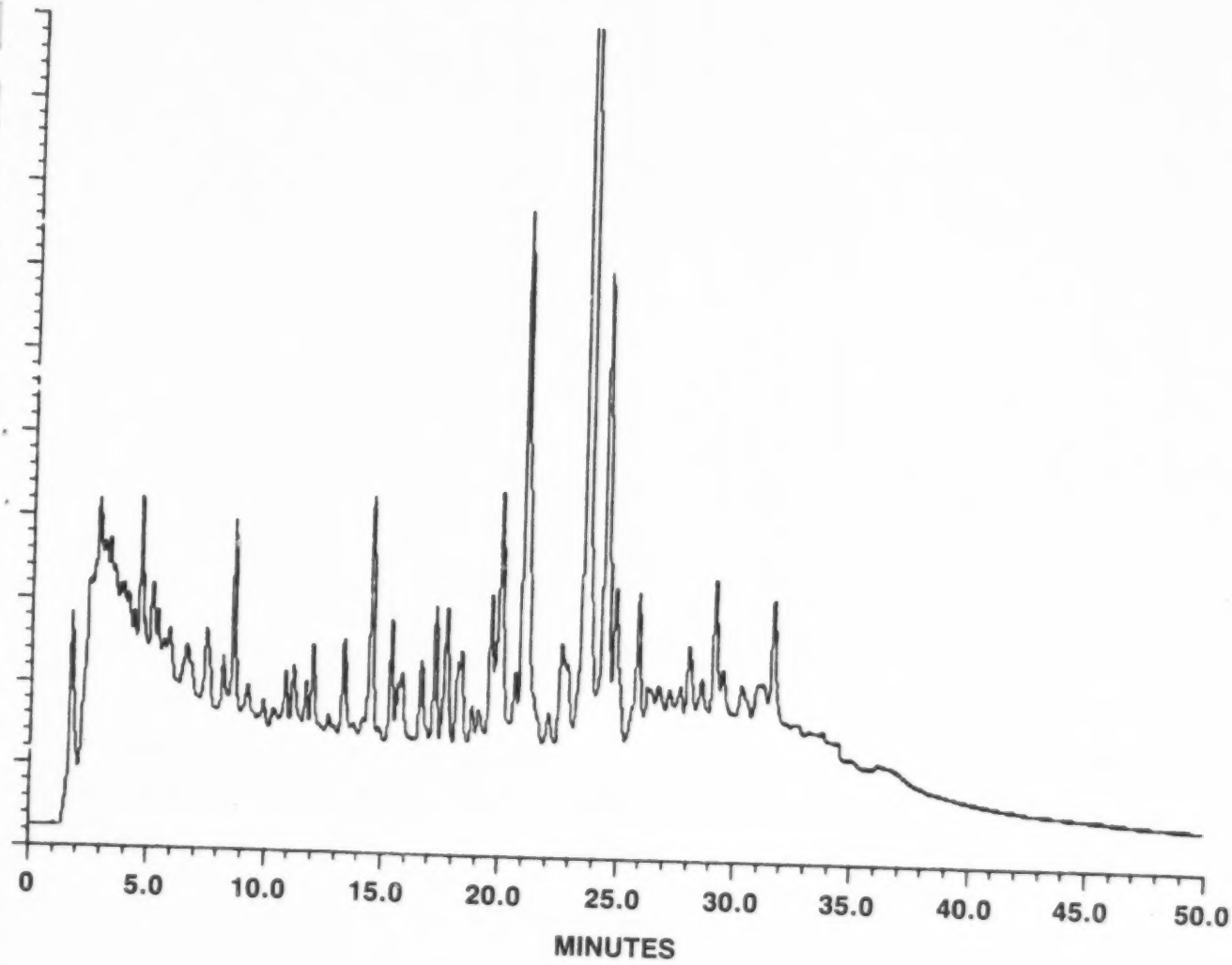

Figure B-3. The chromatogram from HPLC analysis with UV detection of the nonfractionated air particulate extract.

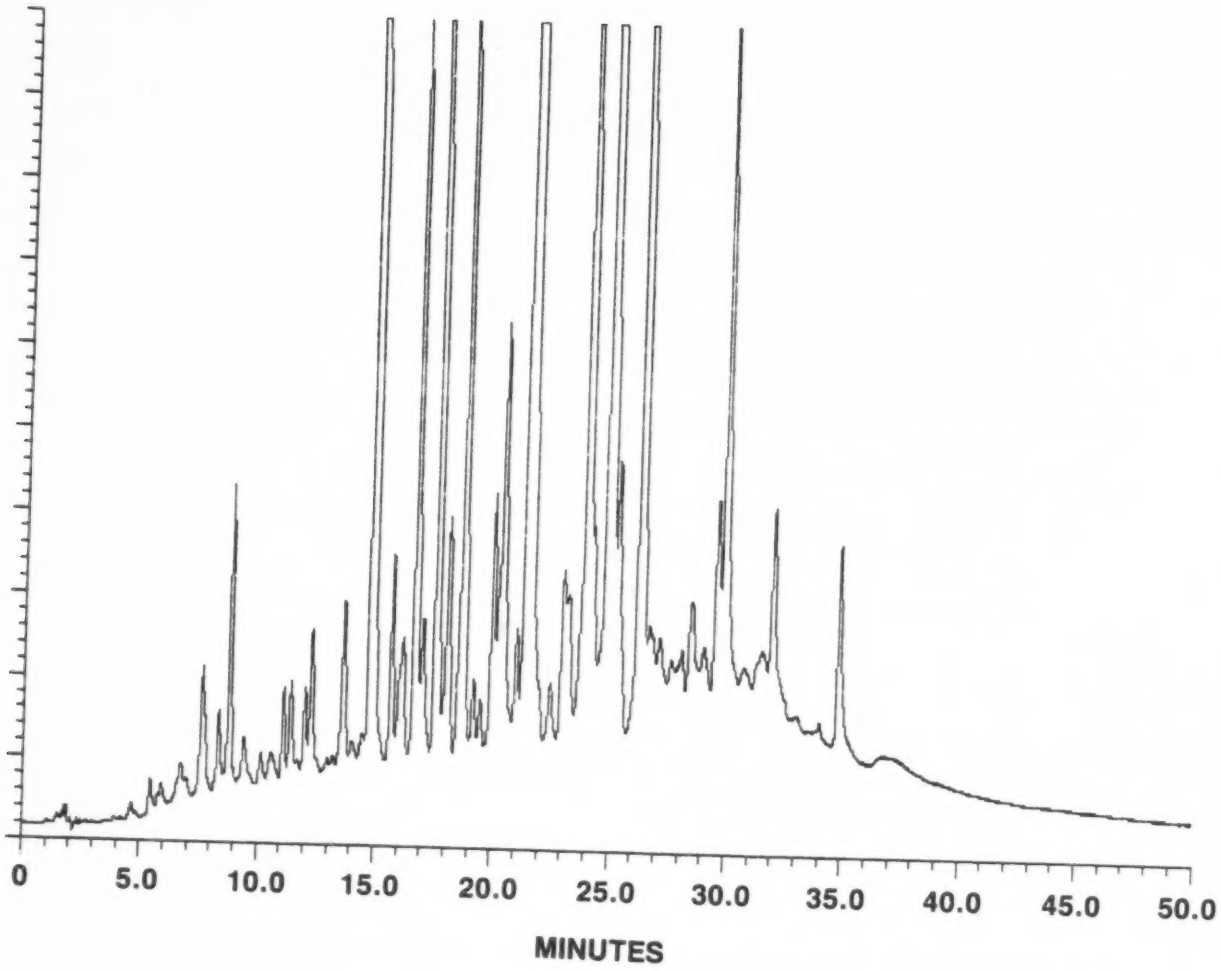

Figure B-4. The chromatogram from HPLC analysis with UV detection of the methylene chloride fraction of the air particulate extract.

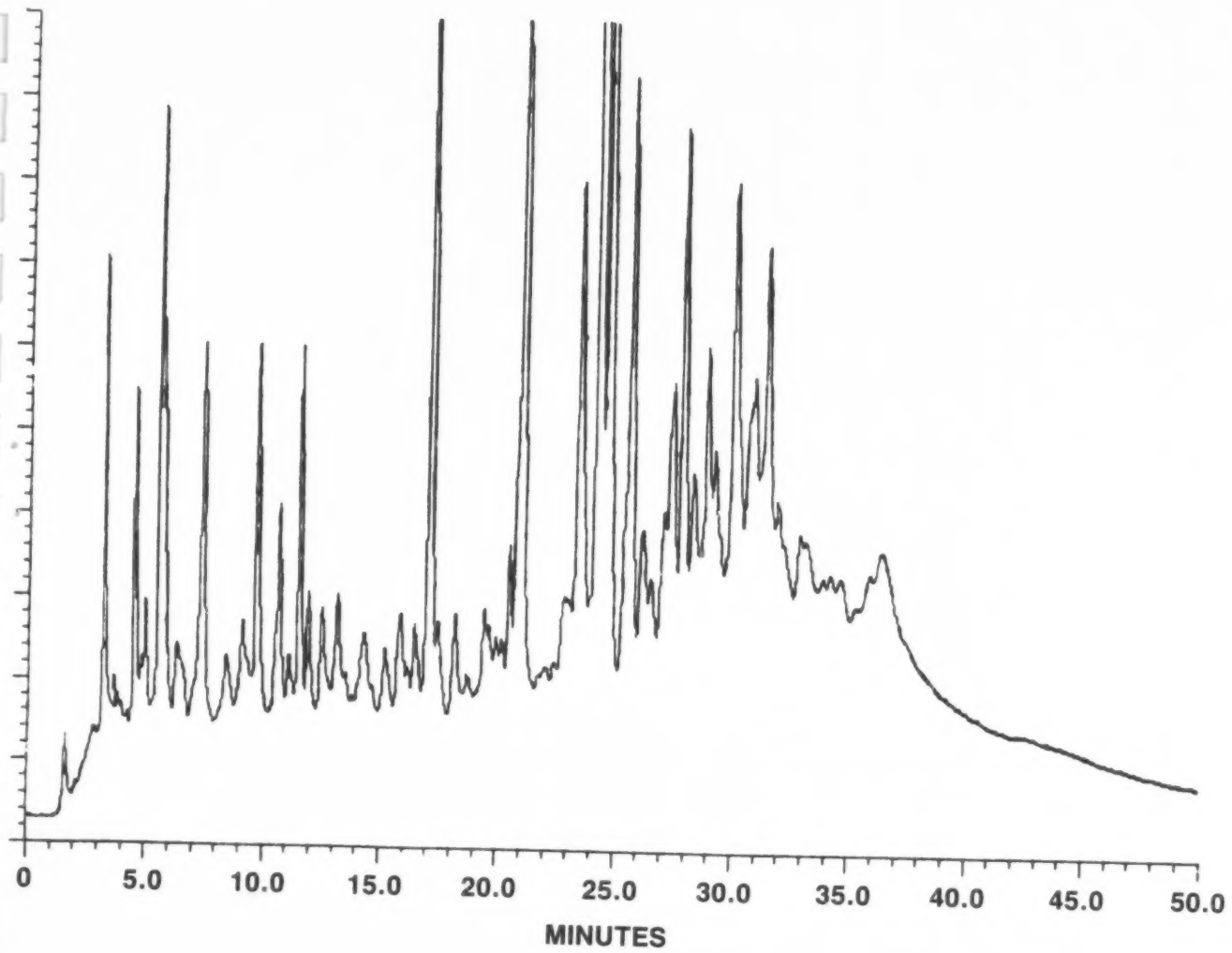

Figure B-5. The chromatogram from HPLC analysis with fluorescence detection of the nonfractionated air particulate extract.

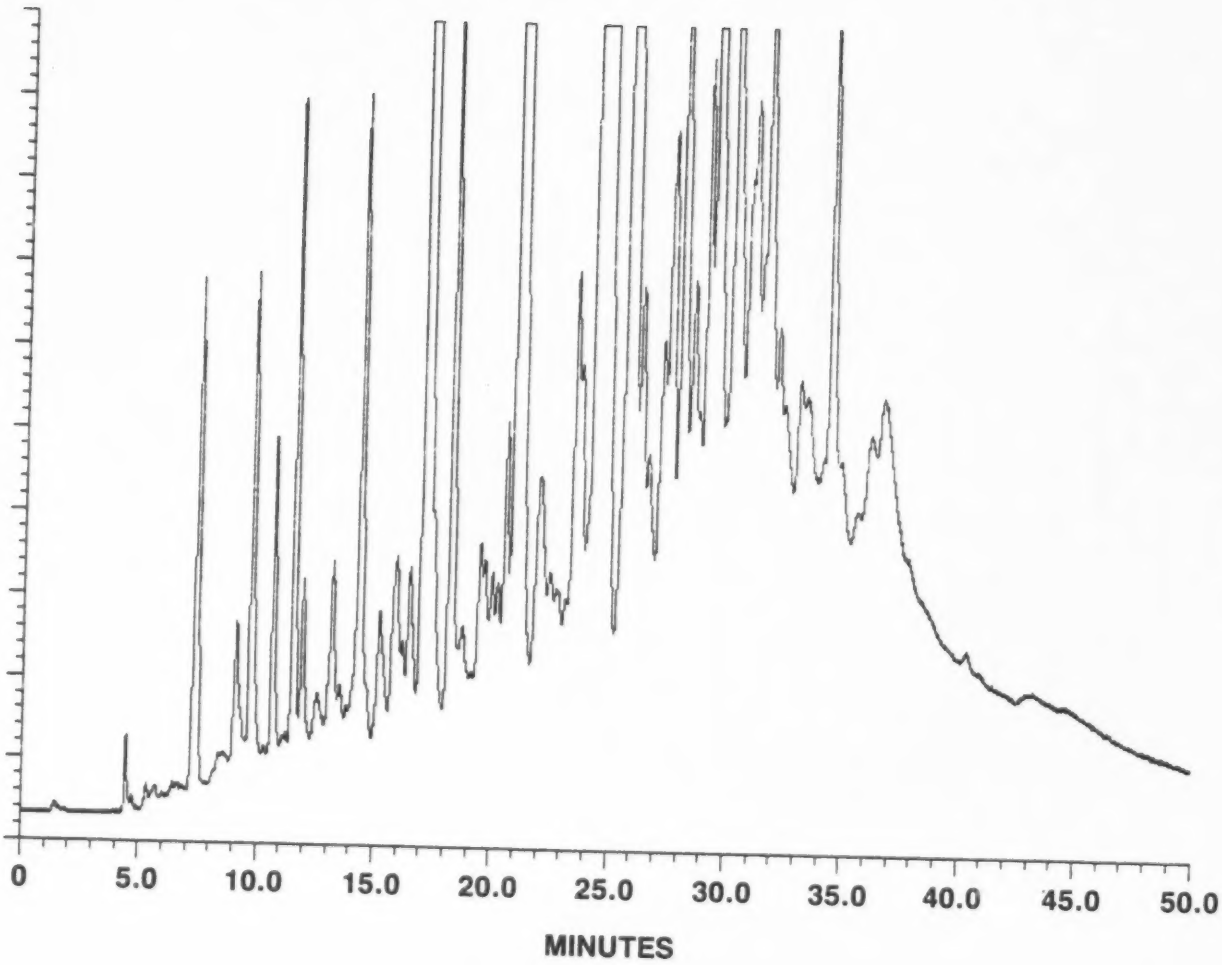

Figure B-6. The chromatogram from HPLC analysis with fluorescence detection of the methylene chloride fraction of the air particulate extract.